RECOMMENDED GUIDELINES FOR SAMPLING MARINE SEDIMENT, WATER COLUMN, AND TISSUE IN PUGET SOUND

Prepared for

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CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CTD	Conductivity, Temperature, Depth (Instrument)
EPA	United States Environmental Protection Agency
HAZWOPER	Hazardous Waste Operations
HDPE	High Density Polyethylene
HSP	Health and Safety Plan
LDPE	Low Density Polyethylene
MTCA	Model Toxics Control Act
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NTU	Nephelometric Turbidity Unit
OSHA	Occupational Safety and Health Administration
PSAMP	Puget Sound Ambient Monitoring Program
PSDDA	Puget Sound Dredged Disposal Analysis
PSEP	Puget Sound Estuary Program
PSP&G	Puget Sound Protocols and Guidelines
PSWQA	Puget Sound Water Quality Authority
PSWQAT	Puget Sound Water Quality Action Team (formerly PSWQA)
PTFE	Polytetrafluoroethylene (Teflon^{TM})
QA/QC	Quality Assurance/Quality Control
SM	Standard Method
SMS	Sediment Management Standards
SOP	Standard Operating Procedure
SPM	Settling Particulate Matter
VHF	Very High Frequency
VOA	Volatile Organic Analysis
WISHA	Washington (State) Industrial Safety and Health Administration

ACKNOWLEDGMENTS

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1. INTRODUCTION

This document presents recommended guidelines for sampling marine sediment, water column and tissue for the chemical analysis of conventionals, metals and organics parameters, as well as microbiological and bioassay testing. The guidelines include recommended sampling methodologies, field health and safety protocols, quality control and quality assurance procedures, and documentation requirements. Many of these procedures are required when conducting sampling activities under one of the Puget Sound regulatory programs.

These guidelines were developed with the assistance of representatives from organizations that fund or conduct environmental studies in the Puget Sound region (Table 1). The purpose of developing sampling guidelines is to encourage the use of standardized methods by organizations and individuals involved in data generation activities in support of the various Puget Sound monitoring and regulatory programs. The use of standardized field sampling and measurement methodologies should aid in producing comparable data among future studies performed in Puget Sound.

This document presents recommended guidelines for sampling sediment, water column and tissue in the marine environment of Puget Sound. Information regarding fresh water sampling may be found in other chapters of the Puget Sound Protocols and Guidelines (PSP&G). While this document is by no means exhaustive, the guidelines presented herein will support data generation activities for the following major Puget Sound programs:

- Puget Sound Dredged Disposal Analysis (PSDDA),
- Puget Sound Ambient Monitoring Program (PSAMP),
- National Pollutant Discharge Elimination System (NPDES), and
- Washington State Department of Ecology Sediment Management Standards (SMS).

This document attempts to centralize and improve access to general marine sampling guidelines and field information for a variety of matrices and target analytical parameters. Reference is made to other PSP&G chapters for in-depth guidance on sampling activities that support a particular analytical need. The guidelines presented in this document have been compiled partly from information contained in the field sampling sections of the following Puget Sound Protocols chapters. Where appropriate, this information has been updated and/or amended, and supersedes field and sampling information contained in the documents noted below.

- General QA/QC Considerations for Collecting Environmental Samples in Puget Sound (PSEP, 1986a),
- Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound (PSEP, 1986b),
- Recommended Guidelines for Measuring Organic Compounds in Puget Sound Sediment and Tissue Samples (PSEP, 1989a),
- Recommended Protocols for Measuring Metals in Puget Sound Water, Sediment and Tissue Samples (PSEP, 1989b),
- Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments (PSEP, 1995),
- Recommended Protocols for Microbiological Studies in Puget Sound (PSEP, 1986c), and
- Recommended Guidelines for Measuring Conventional Marine Water-Column Variables in Puget Sound (PSEP, 1991).

It should be stressed that this document provides **guidance** on field sampling methodologies. These guidelines are not intended to take the place of carefully written project planning documents. It should also be noted that some program-specific guidance referenced in this document is subject to change through annual PSDDA and SMS updating and clarification processes such as the Sediment Management Annual Review Meeting.

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2. SAMPLING PREPARATION

This section provides information to consider prior to initiating field work and to aid in planning a successful sampling effort and/or data gathering activity.

2.1 Project Plans

Inherent in the success of any sampling effort is the creation of a project plan. Regulatory programs such as NPDES, PSDDA, SMS, Model Toxics Control Act (MTCA), and Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) all have specific project planning requirements and have available detailed guidance for the creation of project planning documents. In each of these programs, regulatory approval of the project plan is required prior to project implementation. A detailed discussion of project planning requirements may be found in *Recommended Quality Assurance and Quality Control Guidelines for the Collection of Environmental Data in Puget Sound* (PSEP, 1997a).

The need for a statistical approach to sampling should never be overlooked when planning a project. The statistician becomes an integral member in designing a successful sampling and analytical strategy. Another critical member of the project design team is the analytical laboratory that will be analyzing samples collected during the project. Laboratory input is invaluable to the success of the project.

The chief scientist, lead field technician or a designee should thoroughly review the project plan prior to each sampling effort, and all sample handling personnel should be familiar with those criteria associated with their respective tasks. The plan should be checked for completeness and clarity of objectives. Additionally, a designated person at the analytical laboratory(ies) assigned to the project must also review the project plan prior to implementation. Depending on the type of project plan selected, major elements may include:

- identification of scientific party and the responsibilities of each member;
- statement and prioritization of study objectives;
- description of study area, including background information and station locations;
- identification of variables to be measured, and containers and preservatives required;
- specification of analytical methods and data reporting requirements;
- identification of all quality control samples to be submitted with analytical samples;
- brief description of sampling equipment and methods including station positioning technique;
- specific standard operating procedures (SOPs) addressing the collection of representative samples;
- proposed cruise schedule (including time, date and location of embarkation and debarkation);
- sample storage, handling, shipping and chain of custody procedures;
- identification of onshore laboratories;
- survey vessel requirements (e.g., size, laboratory needs, sample storage needs); and
- location and availability of an alternate survey vessel.

Project objectives and their prioritization should be understood by all members of the scientific party. This will ensure that if project plan modifications become necessary in the field, their impact on project objectives can be evaluated adequately. After the project plan has been reviewed, contingency plans should be outlined. These plans should include potential problems and their solutions.

The captain of any vessel involved in the field work should be provided with a copy of the project plan to ensure that it is consistent with the equipment and capabilities of the vessel. Modifications to the ship or cruise plan may be required.

To ensure that all required sampling equipment and supplies are available at the time of sampling, an equipment checklist should be developed. Spare parts and backup supplies should be included in the inventory.

2.2 Station Positioning

Proper station positioning is a critical component of sampling and data collection. Successful station positioning allows samples or data to be precisely collected from predetermined locations as well as allowing repeated sampling or data collection at the same location over time. Detailed descriptions of station positioning methodologies and techniques are addressed in the document *Recommended Protocols for Station Positioning in Puget Sound* (PSEP, 1998).

2.3 Health and Safety

The health and safety of the sampling team is a primary concern during sampling operations. The process for addressing these topics should be organized, comprehensive and well documented while ensuring that such concerns do not interfere with the collection of quality data.

Certain projects will require the preparation of a site-specific Health and Safety Plan (HSP) as part of the project planning process. A HSP is required for sediment sampling at sites listed under one or more of the following:

- Model Toxics Control Act (MTCA),
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and
- Sediment Management Standards (SMS)

A HSP is also required for any other area that is known to be contaminated by toxic materials. Requirements for HSPs are provided by the Department of Labor and Industry and detailed in Washington Industrial Safety and Health Administration/Occupational Safety and Health Administration (WISHA/OSHA) regulations. **Health and safety issues are addressed in Appendix A to this chapter.**

2.4 Sampler Design

A large selection of sampling devices is available for collecting marine sediment, water column, and tissue samples. Sampling program requirements, along with a knowledge of individual sampler characteristics, will aid in determining which type of device should provide the best performance. The types of sampling equipment described below represent those samplers that are most frequently used in the marine waters of Puget Sound.

2.4.1 Sediment

The main objective of sediment sampling is to obtain a sample that is closely representative of the environmental area of interest. Sediment sampling devices may be placed in one of three categories: 1) grabs and snappers, 2) corers, and 3) dredges. While most of these larger units are typically attached and deployed from a floating platform, small sample aliquots may be collected by hand if there is little or no overlying water. Sediment material may also be collected while it is still in the process of settling, usually through the use of sediment traps. In some instances, subtidal sampling by divers may be desirable. Since there are no widely accepted protocols available for diver collected sediment sampling, development of, and adherence to, detailed quality assurance and quality control procedures is essential for this type of sampling. If diver collected sediment samples are being collected for regulatory purposes, the sampling plan should be discussed with the appropriate regulatory agencies before samples are collected to ensure the proposed protocols are acceptable.

2.4.1.1 Grab Samplers

Ideally, grab samplers should be able to collect an undisturbed bottom sample with minimal disruption to the surface layer. The typical grab sampler, regardless of type, is held in the open position during descent and activated upon reaching the bottom. The body is usually weighted to help with penetration. Some designs, such as the Smith-McIntyre, Birge-Ekman, and a variety of small spring loaded snapper grabs, will rely on spring tension to close a set of jaws around a given volume of sediment. Other models, such as the following, will incorporate another means of mechanical advantage for enclosing the sediment material just prior to retrieval.

Campbell and Petersen grabs both utilize a pulley arrangement to gain extra purchase to activate a pair of jaws. Shepard (1973) reports that a large Campbell grab was successfully used on continental shelf operations off the east coast, and that large Petersen grabs have been known to bring back undisturbed samples that still retain stratification characteristics. However, Schlieper (1972) points out a potential weakness with the Petersen grab design: the tensile closing action from the attached hydrowire creates a secondary lifting force at the central axis that the two jaws pivot around, resulting in a shallower bite (5 centimeters (cm) or less), especially in firmer sediments.

One of the most commonly used grab samplers for surface sediments in Puget Sound is the 0.1 square meter (m^2) modified van Veen (a smaller 0.05-m^2 sampler is also used, especially on smaller boats with a lighter lifting capacity). The van Veen is popular because, despite its compact size and weight, it is capable of collecting sediment material up to 17 cm in depth. The unique scissors-like closing action generated by the lifting wire provides good leverage while helping to further embed the jaws into the sediment. It is not unusual to penetrate down to 5 to 10 cm, even in firm, sandy bottom material. The sampler also has large access doors for convenient removal of the upper sample layers. The mesh covering on the sampler doors allows water to pass through during deployment, reducing the pressure wave that can disturb the floc layer on the surface of the sediment.

All grab samplers run the risk of sample leakage if rocks or other debris are present that are capable of preventing complete closure of the jaws. The Orange Peel Bucket sampler is an attempt to get around this problem. It utilizes four spade-shaped jaws which are less susceptible to jamming, making it sometimes more desirable for very rocky environments. However, the additional seams from the multiple jaws often allow significant sample loss and/or disruption of the finer-grained sediments during ascent.

Instead of jaws, Holme and Shipek samplers utilize one or two rotating semi-circular scoops to collect sample material. A mechanical advantage is employed via the lifting wire to rotate the scoops after the sampler has settled on the bottom. A major disadvantage is that the 180-degree rotation of the scoop severely disrupts the stratified configuration of the material.

2.4.1.2 Coring Devices

Sediment coring devices are designed to collect samples that give an accurate representation of sediment stratification over depth. All suitable coring devices must contain the following components:

- a rigid core tube (with or without core liner),
- a one-way water vent at the top of the core tube,
- a cutting edge (cutter) at the bottom,
- a mechanism for sample retention (e.g., core catcher, flaps, etc.) just above the core cutter, and
- a means for driving the tube into the sediment to a predetermined depth.

Coring devices typically used in Puget Sound fall into one of six basic categories: 1) gravity, 2) box, 3) piston, 4) impact, 5) vibrating, and 6) diver-assisted. Selection of the most appropriate coring system is generally driven by project needs, cost limitations and composition of the sediments to be sampled.

A gravity corer is a simple core tube, weighted at the top end, which free falls over an established distance to penetrate the bottom. As an example, the Phleger corer can collect a core down to a depth of approximately four feet. Gravity is the only driving mechanism, and some designs incorporate tail fins to help stabilize the device during the drop. The free fall is usually controlled by use of a tripping mechanism-and-counterweight assembly which precedes the core tube by a calculated number of feet. Some advantages to this system are that it is relatively inexpensive, has essentially no moving parts and is easy to operate. Disadvantages include structural distortion of the strata due to internal frictional compression from the tube itself, the potential for dewatering (which could skew porosity and/or bulk density results) and limited penetration depth of just a few feet.

The Reineck box corer uses an open-ended rectangular box, found in various sizes, in place of a core tube. The dimensions of the box are large enough that the surface of the sediment remains essentially undisturbed during the collection process. Upon reaching the bottom, the weighted box slides down through the support frame and penetrates the sediment. The lifting wire uses the mechanical advantage of a pulley system to swing a spade-like knife through the sediment to close off the lower end. Two hinged covers at the top seal off the upper opening. The box corer takes excellent, undisturbed samples, even in compact material. However, it is not suitable for small boats as it weighs about 900 pounds and is awkward to handle.

The piston corer, such as the Kullenberg corer (or modification thereof), is essentially a gravity corer with the addition of an internal piston. The lifting wire is attached to this piston, rather than the tail of the corer. Upon impact with the bottom, the piston stops while the core tube continues down through the substrate. Upon retrieval, the piston creates a negative hydrostatic pressure against the surface of the sediment which aids in extraction of the material as the tube is withdrawn. Some advantages include improved penetration depth (the original design was capable of 65 feet of penetration in some substrates), and minimal sediment compression. Disadvantages include some loss of the uppermost surface layer (due to bow wake from the piston-plugged nose during descent) and the corer may be somewhat cumbersome to operate.

Impact coring utilizes a concussive force to drive the core tube into the substrate. It is used primarily on compacted sediments where gravity and piston corers have little effect. The core tubes must be of a sturdy material. An advantage is good penetration in firm substrates such as those having a high clay content. The main disadvantage is its relative expense, requiring a stable floating platform with a large enough work area to supply the core-driving and support equipment.

Vibration or vibra-coring, like impact coring, uses an external driving force to penetrate sediments that are unsuitable for simpler coring devices. In essence, the vibrational force liquefies the substrate in the immediate vicinity of the core cutter, allowing the core tube to enter the bottom. An advantage is good penetration in firm, sandy substrates and/or those containing a large amount of small-sized debris. A disadvantage is the relative expense, as a stable floating platform with a work area large enough to maneuver and deploy the potentially awkward vibra-coring device is required.

Diver-assisted coring employs divers who drive the core tubes directly into the sediment substrate with the aid of either mechanical or pneumatic hammers. The diver is usually responsible for noting the inside and outside depth penetration measurements, plugging the tube against sample leakage, and attaching the lifting line. One advantage is that the diver may be able to supply additional observations. The disadvantages are that diver-assisted operations are expensive, and the operation is limited by diver depth and endurance limitations.

2.4.1.3 Dredging Equipment

Dredges are towed devices that collect rock and biological samples along, or just beneath, the surface of marine sediments. For geological applications, Shepard (1973) states that the pipe dredge and the frame dredge are traditionally the two most common devices for collecting rock samples from the sea floor. For sediment collection, they are significantly inferior to coring and grab samplers due to sample loss through the coarse-mesh bag, and total disruption of the remaining material. For this reason, this type of equipment will not be discussed further.

2.4.2 Water Column

The main objective of water column sampling is to obtain representative samples from discrete depths at an established sampling point. Water column samples are usually collected with some type of water bottle sampler. These samplers typically consist of a cylindrical tube with stoppers at each end, along with a closing device that is activated from the surface by a messenger or an electrical signal. Niskin, Van Dorn and Kemmerer samplers are some of the samplers most commonly used in Puget Sound. Multiple water samplers may be either sequentially attached to a hydrowire so that several discrete depths can be sampled during one cast, or they may be mounted on a rosette-type frame, which allows replicate sampling at the same depth. Water samples may also be collected with a pump, the intake of which has been deployed to a known and desired sampling depth.

Regardless of the sampler type, it should have sufficient capacity to supply adequate volume for the tests required. It is also important for inner surfaces that come in contact with the sample to be made of inert, noncontaminating materials.

2.4.3 Tissue

Some project objectives may require that laboratory analyses be conducted on tissue samples from specific marine organisms. Over the years, a large assortment of sampling equipment has been developed to collect marine animals from essentially every major taxonomic group. The preferred method for sample collection will be determined by the type of organism required, and the nature of its habitat.

Primary concerns when collecting marine animals for chemical analyses are that:

- specimens be representative of the population being sampled,
- specimens be representative of the geographic area being sampled,
- metabolic changes be minimized during transit between the sampler and the lab bench, and
- sample integrity be preserved.

2.5 Cleaning Methods for Field Equipment and Sample Containers

Proper cleaning of both sampling equipment and containers will enhance the representativeness of a sample by ensuring that detectable analytes are sample-related rather than equipment-related.

2.5.1 Sampling Equipment

The following procedures for cleaning sampling equipment are general and can be used successfully in most sampling situations. Specialized sampling equipment that requires additional cleaning procedures is described in detail in other sections.

2.5.1.1 Field Decontamination of Sampling Equipment

Field decontamination of sediment sampling equipment and associated utensils should be conducted between sampling stations by scrubbing with a brush and phosphate-free detergent solution to remove excess sample material. All equipment should then be thoroughly rinsed with clean *in situ* water, using either a clean hose while on deck, or by repeatedly submersing the equipment overboard. It is desirable to give the sample-handling utensils a secondary rinse with analyte-free water. At contaminated sites with high concentrations of organic compounds, a solvent rinse may also be necessary prior to the final analyte-free water rinse.

The most suitable detergents would be those that leave the least amount of residue behind, especially residue containing analytes that could bias sample results. A disinfecting detergent may be required if sampling equipment will be used for collection of samples for biological analysis. Analyses may need to be performed on one or more container blanks and/or rinsate equipment blanks to determine which detergents are best (see Sections 3.7.1 and 3.7.4). Acceptable detergents include Alconox™, Liquinox™, and Detergent 8™.

For projects where sediments are expected to be relatively clean, solvent or acid decontamination in the field is not recommended due to the potentially hazardous nature of these chemicals; their introduction into the sampling environment should consequently be avoided. At more contaminated sites, particularly where organic contamination is expected to be high, it is acceptable to use methanol, acetone, or a 50:50 acetone/hexane mix as a rinse for sampling utensils, as these solvents pose less of a threat to personnel and the environment. Decontamination with solvents should always be performed on an open deck of a vessel or outdoors if on land. If trace metals analysis is to be performed on samples, a weak dilution of nitric acid (10 percent HNO_3) may be used as a rinse. All solvent and acid rinses should be followed by thorough rinses with analyte-free water. All decontamination fluids that include solvents or acid rinses should be properly contained and not allowed to enter the environment. Evaporation of small amounts of residual solvent into the air is acceptable.

A tiered approach may be taken to equipment decontamination for sediment sampling when the expected level of contamination is known in advance.

- If the sediment represents ambient conditions, decontamination may consist of merely scrubbing the sampling equipment to remove residual sediment followed by a thorough rinsing with *in situ* water.
- If the sediment is slightly contaminated, decontamination may consist of scrubbing with a water and phosphate-free detergent mixture, followed by rinses with *in situ* water and analyte-free water.
- If the sediment is heavily contaminated, decontamination may consist of scrubbing with a water and phosphate-free detergent mixture, a rinse with *in situ* water, rinses with solvents and/or acids, and a final rinse with analyte-free water.

Another option would be to have additional sets of precleaned sampling utensils on board so that a fresh set could be used at each new sampling station. Advantages are that decontamination could be conducted under more controllable conditions on shore, cleaning time would be minimized between stations and there would be little onboard need for solvents and/or acids.

Field decontamination of water sampling bottles should consist of thoroughly rinsing the bottle analyte-free water followed by a thorough *in situ* rinsing.

2.5.1.2 Laboratory Decontamination for Conventionals Analysis

For conventionals analysis, sample collection equipment should be cleaned with a phosphate-free detergent solution, followed by thorough rinses with hot tap water and analyte-free water. If oil and grease analysis is required, equipment should also be rinsed with acetone or methanol in a well-ventilated area. If ammonia and nitrate/nitrite analysis is also required, a sulfuric acid dilution (20 percent H_2SO_4) is to be used instead. HNO_3 is somewhat more effective as a decontaminating agent, but it is known to interfere with nutrient analyses. The acids used should be of at least reagent-grade purity.

2.5.1.3 Laboratory Decontamination for Metals Analysis

Prior to use, sampling and laboratory equipment should be thoroughly cleaned with a phosphate-free detergent solution, rinsed thoroughly with hot tap water, soaked a minimum of one hour (overnight is recommended) in 20 percent HNO_3, and then rinsed with analyte-free water.

If sampling equipment contains metal components, those parts should be cleaned as stated above, but the acid-soak step should be omitted. If both trace organics and metals analyses are to be performed on the same samples, final rinsing of metal equipment parts with methylene chloride is acceptable.

If trace metals analysis is to be conducted on marine water, the water sampling bottles must not contain metal or rubber parts that could potentially contaminate the water sample. The sampling bottles should be cleaned by first filling them with 20 percent HNO_3 for at least 24 hours, followed by thorough rinsing with metal-free water.

2.5.1.4 Laboratory Decontamination for Organics Analysis

For trace organics analyses other than volatile compounds, sample collection equipment should be cleaned with a phosphate-free detergent solution, followed by thorough rinses with hot tap water and analyte-free water. Before use, equipment should be rinsed with solvent (e.g., acetone, hexane or methanol) and air-dried. If samples are to be analyzed for volatile compounds, sampling equipment should be oven-dried at 105°C or greater after the wash and water-rinse steps. A solvent rinse should be avoided to eliminate the possibility of analytical interferences. A 20 percent HNO_3 soak may be used instead of the solvent rinse.

2.5.2 Laboratory Cleaning of Sample Containers

Various Puget Sound marine sampling programs and published analytical methodologies specify sample container criteria, relative to the analytes of interest. Selection of sample container types should meet the prescribed data quality objectives, while following criteria for the Puget Sound program guidelines under which the project is carried out. They should also be specified in any project plan documents. Documentation of sample container cleanliness may be required by a project and, if so, such documentation should accompany samples throughout sampling and analysis. Proper sample containers for sediment, water, and tissue samples are summarized in Tables 2, 3, and 4.

If the analytical laboratory under contract reuses sample containers, the following sample cleaning procedures should be verified as part of the project planning process. Cleanliness should be verified by the collection and analysis of container blanks (see Section 3.7.1). If this information is critical, bottle blanks may be prepared and analyzed prior to field activities. Many precleaned sample containers are shipped from the manufacturer with Environmental Protection Agency (EPA)-certified levels of cleanliness. The certification provided with the sample container shipment will outline the cleaning procedures performed by the manufacturer to receive the certification. This information should also be reviewed as part of the planning process prior to the start of field sampling activities. Depending on the matrix to be analyzed, recleaning and reuse of sample containers may be impractical. In such situations, it may be necessary to use certified pre-cleaned containers.

2.5.2.1 Conventionals

Sample containers and lids used for conventionals analysis should first be washed with a phosphate-free detergent solution, followed by thorough rinses with hot tap water and analyte-free water. For oil and grease analysis, an additional rinse with hexane or methylene chloride and drying at 105°C for 30 minutes should be added to the procedure.

2.5.2.2 Metals

For trace metals analysis, new sample containers should always be used. Sample containers and lids should be thoroughly cleaned with a phosphate-free detergent solution, thoroughly rinsed with metal-free water, soaked for 24 hours in 20 percent HNO_3 or 50 percent HCl, and rinsed with metal-free water. The acids used should be of at least reagent-grade purity. See section 2.3 of *Recommended Guidelines for Measuring Metals in Puget Sound Marine Water, Sediment and Tissue Samples* (PSEP, 1997b) for additional information about cleaning methods.

2.5.2.3 Organics

Sample containers and lids used for semivolatile analysis should first be washed with a phosphate-free detergent solution, followed by thorough rinses with hot tap water and analyte-free water. The last step should be an acetone rinse, then a final rinse using high-purity methylene chloride. The lids should be in place on the container during this rinse step (solvent in the container with the lid tightly screwed down) because the solvents may rinse plastic from the interior screw threads onto the Teflon™ lining. Firing of glass containers at approximately 350°C for 4 hours may be substituted for the final solvent rinse only if precautions are taken to avoid contamination as the container is dried and cooled.

For analysis of volatile organic compounds, sample containers, screw caps, and cap septa (silicone vapor barriers) should be washed with a phosphate-free detergent, rinsed once with tap water, rinsed at least twice with analyte-free water, then dried at greater than 105°C. A solvent rinse should generally be avoided because it may interfere with the analysis, although a methanol rinse may be acceptable. See section 2.3 of *Recommended Guidelines for Measuring Organic Compounds in Puget Sound Water, Sediment and Tissue Samples* (PSEP, 1997c) for additional information about cleaning methods.

2.5.2.4 Microbiology

Sample containers for the collection of microbiological parameters should be washed with a phosphate-free detergent, triple rinsed with hot tap water and autoclaved for a period of at least 15 minutes at 121° C and 15 pounds. Sample containers for the collection of toxicological testing samples should be washed with a phosphate-free detergent, triple rinsed with hot tap water and may be finished with a weak hydrochloric acid rinse.

3. SAMPLING PROCEDURES FOR SEDIMENT

This section describes recommended procedures for collection of surface and subsurface marine sediments.

3.1 Sediment Grabs

Grab samplers are used to collect surface sediments. In some cases, not all of the sample material within the sampler is utilized. For instance, source control and ambient monitoring sampling programs might be interested in performing trend analyses for recently deposited sediments, in which case only the top 2 cm might be required for analysis. For sediment cleanup efforts, it is now a standard practice for all sampling programs to require that the top 10 cm be retained for evaluation.

3.1.1 Sampling Procedures

There are several kinds of grab sampling devices that could be used to sample marine sediments in Puget Sound (Section 2.4.1.1). The primary criterion for selection of an adequate sampler is that it consistently collect undisturbed samples to the required depth below the sediment surface without compromising the sample material. Such a sampler should:

- be made of contamination-free materials,
- create a minimal bow wake when descending,
- enclose the sample material with minimal disturbance,
- form a leakproof seal during sampler retrieval, and
- have easy internal access to the sample surface.

Puget Sound marine sediment is commonly collected with a 0.1-m^2 Van Veen grab sampler, especially for those samples undergoing chemical analysis for regulatory purposes. Nonstandard sampling devices may be proposed for use but, if data will be used for regulatory purposes, their use must be approved in advance by the regulatory agency. Such devices should be designed to meet the criteria outlined above. A smaller 0.05-m^2 sampler may also be used, although there will obviously be less material, and a shallower penetration can be expected. Stainless steel is considered to be the material of choice for the main body of the Van Veen grab. Because good-quality stainless is very resistant to the corrosive effect of salt water, it will release minimal quantities of free ions, and its relatively nonporous surface will make decontamination easier.

To better meet the above requirements, a 0.1-m^2 Van Veen grab sampler can be slightly modified as follows.

- The small secondary lifting chain which holds the jaws open during deployment sometimes falls into the jaw hinge after release, causing it to jam. This problem can be alleviated by replacing it with a stiffer, two-legged bridle made of stainless steel hydrowire.
- The wire screen on the upper access doors is lightly spot welded in place. These welds can fail over time, resulting in possible sample loss, or loss of the entire screen and neoprene flap assembly, thus disabling the sampler until a replacement door can be installed. One solution is to overlap the screen spot welds with an additional strip of stainless steel and bolt to the door frame. Also replace all regular nuts with (stainless) locking nuts.
- To form a tighter seal between the upper doors and the main body of the grab, lay down a bead of

good-quality silicone sealant at the top where the two surfaces meet. Let the sealant cure for a few days with the doors open (silicone is totally inert in sea water and will not bias sample results).

- Each access door on the Van Veen has its own neoprene flap. If the flap is too flimsy, it could fold back on itself during retrieval, causing sample washout. The flaps can be made more rigid by laminating additional neoprene strips (at least 1 inch wide) around the three upper edges of each. The neoprene cement should be allowed to cure a few days before using. If the flaps are too heavy, however, the pressure wave created during descent could increase.
- If two grabs are to be deployed in tandem (through use of a spreader bar), use them as independent units; do not bolt them together or join them on a common hinge pin. This way, if one fouls during the tripping sequence, it will not foul the other, thereby increasing the chances of at least one acceptable grab on any given cast.

The grab sampler should be attached to the hydrowire via a ball-bearing swivel, as all wire rope will have a tendency to twist when strain is applied. During deployment, the safety pin should be released just after the device is clear of the vessel. With the sampler at the surface, the meter wheel, which reads depth below the surface, should be adjusted to zero.

The sampler is lowered at a controlled speed of approximately 4 feet per second with the hydrowire at a straight angle. Under no circumstances should the grab sampler be allowed to free fall to the bottom as this may result in premature triggering, an excessive bow wake, or improper orientation upon contact with the bottom. As the sampler descends, water should be able to pass freely through the closed upper screened doors to minimize the bow wake. Descent speed should be slowed to about 1 foot per second as the sampler nears the bottom to minimize disturbance of the surface sediments. The winch operator should be supplied with bottom depth information so that s/he knows when to reduce winch speed. Once the sampler reaches the bottom, the hydrowire should not be allowed to slack.

After the sampler has been tripped, it should be raised slowly off the bottom to allow for proper closure without spillage. Once clear of the bottom, the ascent speed can be increased to approximately 4 feet per second. Retrieval of the sampler should be continuous. While ascending, the upper door flaps should seal tightly to minimize sample disturbance. The sampler should be handled carefully, especially during rough weather, to minimize sample disturbance. It should also exhibit minimal leakage when coming on board, which is a good indication that the sample was collected in its entirety.

During retrieval, one crew member should watch for the appearance of the sampler, and should alert the winch operator and the vessel skipper when the sampler is first visible below the surface. The winch operator should minimize swinging before the grab sampler is brought on board. Hard hats and gloves should always be worn when handling the grab sampler.

The grab sampler should be decontaminated between sampling stations (see Section 2.5.1.1). If information regarding contamination levels within the sampling area is available, it is recommended that samples be collected from stations starting from the least contaminated and ending with the most contaminated.

3.1.2 Field Sample Handling

After the grab sampler has been secured on board, the upper doors are opened and the sample is examined for acceptability as follows:

- the sampler is not overfilled, which could be indicative of sample loss;
- overlying water is present indicating sample integrity;
- the sediment surface appears to be relatively undisturbed; and
- the desired sample depth has been achieved (ideally, at least 1 or 2 cm should remain at the bottom of the sampler after the upper layer has been subsampled).

If sample acceptability criteria are met, overlying water is carefully siphoned off (if the water is turbid, it could be allowed to settle out for a short period). During or before the sample material is removed, field measurements and observations should be noted and recorded, if required. Field measurements may include sample depth, pH, Eh (redox), specific conductivity, pore water salinity and field screening for grain size. Observations may include a determination of visual/textural soil characteristics and descriptions of visible infauna, the presence of debris, and evidence suggesting the presence of contaminants such as an oil sheen, paint chips, etc..

For subsampling, a sample aliquot is collected to the appropriate sediment depth and placed in a mixing container, such as a stainless steel bowl. It is recommended that sample aliquots be collected with stainless steel utensils such as spoons, spatulas, or ‘cookie cutters’ although PTFE (Teflon™) implements may be substituted. Sample material should be thoroughly homogenized prior to splitting into separate sample containers. If sample aliquots are to be collected from multiple sampler deployments, the stainless steel bowl containing the sediment should be covered between deployments to minimize contamination from the immediate environment and stored in an ice chest or cooler. A successful sampler deployment with a 0.1-m^2 Van Veen grab will yield enough material from the upper 2 cm to fill about three 8 oz. jars. Sample aliquots for physical, chemical and biological testing should always be collected out of the same grab sample or composite of grab samples.

Sample material for volatile organic or sulfide compound analysis must be collected out of the grab sampler from the first successful deployment and sample containers must be filled immediately, prior to any homogenization. Sample containers for volatile analyses should have no headspace. Once the volatile subsamples have been removed, the sample is thoroughly homogenized with a stainless steel utensil until a uniform color and texture are achieved. After homogenization, the remaining subsamples are transferred to appropriate containers and preserved as required. Samples that are to be stored frozen require a minimum of 2 cm of head space in the sample container. Storage requirements are summarized in Table 2.

In accordance with United States Coast Guard regulations, sediment retrieved from grab samples that exhibits evidence of contamination such as a strong odor or visible sheen should not be disposed of overboard. The sediment should be contained and removed off site for proper disposal as potentially dangerous or hazardous waste.

3.1.3 Sample Depth

The depth to which surficial samples are collected will be project and program specific and should be specified in the project planning document. Some considerations are listed below.

Past studies in Puget Sound have demonstrated that the majority of benthic infauna are generally found within the uppermost 10 cm of the sediments. While some species may be present at greater depths, 10 cm is generally assumed to represent a reasonable estimate of the biologically-active zone. Determining site-specific vertical distribution of benthic infauna or the depth to anoxic sediments is generally not practical. Sediments at possible cleanup sites must be collected to a depth of 10 cm to allow for comparison to the applicable Sediment Management Standards criteria.

In some cases, monitoring data may be used to help interpret temporal changes in sediment conditions. For example, some programs are designed to monitor ambient conditions, various permitted discharge points or a cap placed over contaminated sediments as part of remediation. In such cases, it is appropriate to limit sample collection to the uppermost 2 cm of sediments. A depth of 2 cm is generally considered to be the average sediment thickness accumulated over a one-year period throughout the depositional areas of Puget Sound.

3.2 Sediment Cores

Sediment cores are collected to evaluate chemical and/or biological characteristics of surface and subsurface sediments at depths which greatly exceed those achieved by grab samplers. Selection of the most appropriate coring device usually depends on:

- the quantity of sample required within a given stratification (determines diameter size),
- the penetration depth required,
- the sediment characteristics (e.g., soft, compact, rocky, etc.), and
- possible physical restrictions pertaining to deployment (i.e., vessel size, lifting capacity, etc.).

3.2.1 Sampling Procedures

Regardless of the coring method employed, the core tube should be constructed of a noncontaminating material which would not contribute analytes of interest to the sample medium. If the core tube is designed to hold a core liner, the liner would then need to be constructed of a noncontaminating material. Refer to the appropriate cleaning methods as described in Section 2.5.1.

Prior to deployment, inspect to see that the sediment retainer behind the cutting edge will provide a good seal. If the device is a box corer, be sure that the cable feeds through the pulley system properly and that the spade rotates freely. The opening/closing mechanism at the top of the core body should also be checked; it may be in the form of a stop-check valve, a valved piston or a set of doors.

Both gravity and piston corers utilize inertia as the primary driving force to achieve the desired penetration depth. The degree of penetration can be altered by either adjusting the number of weights at the top of the tube or by changing the vertical distance that the core tube is allowed to free-fall. During descent, the device should be lowered under power to its predetermined free-fall distance above the bottom. The lowering should be halted when this vertical distance equals the difference between the meter wheel reading and the fathometer reading.

If the device is equipped with a trip-weight or a small gravity trip-corer, the free-fall distance will equal the length of the core tube plus the vertical distance between the core cutter and the trip-weight suspended beneath it. When the trip-weight contacts the bottom, it relaxes the tension on the release mechanism and the core tube free-falls into the sediment. Consistent penetration depths can be obtained with this method, as the free-fall distance is independent of winch control and changing bottom depth variables.

With smaller boats using simpler coring devices, free-fall can be initiated by free-wheeling the winch drum, but only after the desired free-fall depth has been reached. The winch should be braked immediately after the core tube has penetrated fully. Changes in wire strain can be observed through the use of a tensiometer or dynamometer snatch-blocked to the lifting wire.

The amount of pull that is required to extract a core tube from the substrate depends on the specific gravity of the device and its contents, plus the amount of frictional force against the surface of the core tube walls that must be overcome. This force depends both on the nature of the sediment type (e.g., clay-based material requires more pull), and the depth penetrated. For this reason, the capacity of the lifting equipment should never be underestimated. During the extraction, the wire strain should be steady and continuous; the vessel should be held stationary directly above the coring device. Once clear of the bottom, winch take-up speed may increase to about 4 feet per second.

While swinging the sampling device on board, it should be noted if there is sample leakage at the cutter end. If possible, it may be desirable to place a cap or plug over one or both ends of the core tube. While still vertical, overlying water should be siphoned off at the top of the core tube (after allowing for settling time). The length of the sediment core should then be determined by comparing measurements of the length of the core material against the overall penetration depth (as evidenced by traces of sediment material on the outer surface of the core tube). If the core tube uses a liner, the liner may need to first be removed to establish sample depth. With diver-driven core tubes, it is sometimes possible for the diver to make this depth comparison while the tube is still imbedded. The ratio of penetration depth to core material length should be calculated to determine the compaction of the sediment during coring.

If the core is acceptable, the core tube (or liner) should be labeled with the core identification number, collection date, core orientation and length of core material collected. Until the core sample can be split into sections, the core tube should be secured in an upright position, taking care not to invert the core. The procedures described above are also followed when collecting core samples employing impact or vibrational coring devices.

3.2.2 Field Sample Handling

Cores should be split within 24 hours of collection. The cores should be stored in an upright position and kept cool to the best extent possible between the time of sample collection and sample splitting. Ideally, cores should be refrigerated until splitting is performed. Cores should be stored in a manner that best facilitates chain of custody protocols (Section 6.2).

For transverse sectioning, the core tube (or liner) is placed on a secure surface such as a plumber's tripod or specially designed coring table, and the end caps removed to allow remaining water to run out. The length of the core material is measured again to evaluate further compaction between collection and sectioning. Beginning at the top of the core tube (the sediment surface), sample sections are measured and marked on the outside of the core in indelible ink. Care should be taken when measuring core sections to consider core compaction. Core sections, depending on the material of the tube or liner, may be cut with a manual, heavy-duty pipe cutter. If cutting all sections from the core at one time, cover the top and bottom of each section with aluminum foil to prevent contamination from the immediate environment and to keep the sediment intact.

After cutting, the sediment material can be extruded slowly by tilting the core tube. If the core section will not slide out easily, a plunger may be used to aid the process. The plunger may be constructed of any material, but should be covered with a clean piece of aluminum foil each time it is used. Note any stratification of color or sediment composition on the core-splitting data sheet. To exclude any sediment coming into contact with the wall of the core tube, the outer layer (0.25 to 0.5 cm) of the sediment core should be scraped away using a stainless steel knife or straight-edge. (This material may be used for particle size distribution analysis if additional sediment volume is required.) If volatile compounds (organics or sulfides) are to be analyzed, fill these sample containers immediately. The remainder of the sediment core is placed into a stainless steel bowl and homogenized as thoroughly as possible with a stainless steel or Teflon™ spoon or spatula. Sample aliquots should be transferred to appropriate containers and preserved as required.

Longitudinal core splits are advantageous to better evaluate the various sedimentary stratifications relative to overall structure. In this case, the core tube or liner can be split with a circular saw to expose the core, or the core material can be run across a splitting knife as it is ejected at one end. The same measurements, observations, and sample-handling techniques as those described above should be followed.

Special attention should be paid to regulatory requirements for sample homogenization over depth when sectioning core samples. PSDDA requires homogenization over a certain depth (i.e., 4 feet) to assess chemical and physical characteristics of the depth of sediment that will be dredged. SMS programs are interested in samples that have been homogenized from obvious sediment stratification.

It should be stressed that core samples provide a limited volume of sample. Careful planning is required to provide sufficient sample matrix for the most critical analyses.

3.3 Hand Collection

With a favorable tide, sediment samples (either surficial or at depth) may be collected by hand in the intertidal zone. Care should be taken when collecting samples by hand that sediments are not transported from one station to another on boots, gloves, or sampling implements.

3.3.1 Sampling Procedures

Sediment samples may be collected by hand with a variety of sampling implements such as spoons or trowels for surface sediments, or with hand augers or corers for collecting sediments at discrete depths. Any sampling implement that comes into contact with the sample should be constructed of stainless steel or Teflon™. If individual sample collection kits are not available for each sampling location, sampling equipment should be thoroughly decontaminated between stations by scrubbing with a phosphate-free detergent solution, followed with a thorough rinsing with analyte-free water. While it is not advisable to create the potential to introduce chemicals to the sampling environment, if heavy contamination by organic compounds or metals is expected at the site, sampling equipment may be rinsed with methanol, acetone, or a 50:50 acetone/hexane mix for organics or 10 percent HNO_3 for metals. Decontamination fluids containing solvent or acid rinses should be properly contained and not allowed to enter the environment. All decontamination fluids should be transported off-site at the end of each sampling day.

3.3.2 Field Sample Handling

If at all possible, samples should be homogenized and aliquots transferred to sample containers in the field. If volatile organic or sulfide compounds are to be analyzed, fill these sample containers immediately, prior to homogenization. The remainder of the sample is transferred directly from the substrate to a stainless steel bowl and homogenized as thoroughly as possible with a stainless steel or Teflon™ spoon or spatula. Sample aliquots are transferred to appropriate laboratory supplied containers and preserved as required.

If the these procedures are not feasible in the field, the entire sample should be transported to the laboratory in ice chests as soon after collection as possible. The sample should be kept in a tightly closed, inert glass or metal container (or plastic if no organics are to be analyzed) and be maintained at approximately 4°C until received by the analytical laboratory.

3.4 Sediment Traps

Sampling and analysis of settling particulate matter (SPM) provides useful data for studies of sedimentation rates and resuspension of bottom sediments. SPM may be collected successfully through the use of sediment traps. Sediment traps may include flat containers, bottles, jars, plastic bags, funnels, and cylinders (often containing lids or collars). Cylindrical traps with the appropriate height-to-diameter dimensions appear to be the best instruments to correctly measure the settling downward flux of particulate matter (Mudroch and MacKnight, 1994).

The Washington State Department of Ecology (Ecology) has successfully conducted SPM studies using sediment traps consisting of straight-sided glass cylinders with a collection area of 78.5 cm^2 and a height to width ratio of 5. Ecology has moored paired cylinders for a total collection area of 157 cm^2 (Norton and Michelsen, 1995).

3.4.1 Sampling Procedures

If collecting SPM for chemical analysis, the traps should be cleaned with a phosphate-free detergent solution, then sequentially rinsed with hot tap water, 10 percent HNO_3, analyte-free, pesticide grade acetone, and finally, wrapped in aluminum foil until deployment in the field. If the sediment trap is constructed of plexiglass, the acetone rinse should be avoided as acetone will damage the plexiglass.

Prior to deployment, the traps should be filled with two liters of high-salinity (saturated or nearly saturated) analyte-free water containing a preservative to reduce microbial degradation of the samples during the deployment period. Preservatives may be selected based upon the list of target analytes, and could include sodium azide, formalin, and mercuric chloride.

3.4.2 Field Sample Handling

SPM samples are collected by retrieving the traps and removing the overlying water in the collection cylinders using a peristaltic pump. The water immediately overlying the trapped sediment is analyzed to determine the salinity and the presence of preservative to determine if the trap was disturbed during deployment. The SPM is transferred to sample containers and taken to an analytical laboratory for processing. The particulate fraction of the SPM is removed by centrifuge and split into sample aliquots for chemical analysis.

3.5 Special Considerations

Homogenization is important, especially when the contents from several sediment samplers must be combined to provide sufficient material for testing. The volume of sediment and the number of successful sampler deployments required to meet this volume should be specified during the project planning process. This information should be conveyed to the sampling crew prior to initiation of field activities. Compositing of the contents of multiple sediment grabs may be performed by transferring sediment to a stainless steel or glass bowl and stirring with a clean, stainless steel spoon or spatula until textural and color homogeneity are achieved. Thorough mixing of the sample is required when removing subsamples for different chemical analyses.

Samples collected for the analysis of volatile organic or sulfide compounds should not be homogenized because many of these compounds could be lost while compositing. If analysis of volatile compounds is required, containers should be completely filled with sample sediment from the first grab, prior to sample homogenization. No headspace should remain in either container. To avoid leaving headspace in the containers, sample containers can be filled in one of two ways. If there is adequate water in the sediment, the container should be filled to overflowing so that a convex meniscus forms at the top. Once sealed, the bottle should be inverted; no headspace will be demonstrated by the absence of air bubbles. If there is little or no water in the sediment, jars should be filled as tightly as possible, eliminating obvious air pockets. With the cap liner's PTFE side down, the cap should be carefully placed on the opening of the vial, displacing any excess material.

If sediment chemistry samples are being collected concurrently with sediment bioassay samples, refer to the guidelines included *in Recommended Guidelines for Conducting Laboratory Bioassays on Puget Sound Sediments* (PSEP, 1995). They recommend that all field-collected sediments be homogenized before subsamples are removed for bioassay and chemical analyses (with the exception of volatile compounds that are removed prior to homogenization). This method is used for most studies in Puget Sound, and it ensures that bias to the bioassay or chemical results caused by sample collection and handling procedures is minimized.

3.6 Sample Preservation

Preservation of sediment samples is generally limited to specified storage conditions such as refrigeration or freezing. Depending on the parameter to be analyzed, some samples will require addition of chemical preservatives. Preservation techniques are summarized in Table 2. Care should be taken to avoid exposure to acid gases which might be released when chemical preservatives are added to sediment samples in the field.

Table 2
Recommended Sample Sizes, Containers, Preservation Techniques, and Holding Times for Sediment

Parameter	Minimum Sample Size (g)[a] (wet wt.)	Container	Preservation Technique	Holding Time
Particle Size	100 to 150[b]	Glass or Polyethylene	Refrigerate, 4°C	6 Months
Total Solids	50	Glass or Polyethylene	Freeze, -18°C Refrigerate, 4°C	6 Months 14 Days
Total Volatile Solids	50	Glass or Polyethylene	Freeze, -18°C Refrigerate, 4°C	6 Months 14 Days
Total Organic Carbon	25	Glass or Polyethylene	Freeze, -18°C Refrigerate, 4°C	6 Months 14 Days
Oil and Grease	100	Glass	Freeze, -18°C Refrigerate, 4°C	6 Months 28 Days
Total Sulfides	50 (a 250 ml sample for 5 ml Zn Acetate)	Glass or Polyethylene	Refrigerate, 4°C (2 N Zn Acetate - 5 ml)	7 Days
Acid Volatile Sulfides	50	Glass (no headspace protect from O_2)	Refrigerate, 4°C	14 Days
Total Nitrogen	25	Glass or Polyethylene	Refrigerate, 4°C	28 Days
Biochemical Oxygen Demand	50	Glass or Polyethylene	Refrigerate, 4°C	7 Days
Chemical Oxygen Demand	50	Glass or Polyethylene	Refrigerate, 4°C	7 Days
Volatile Organics	50	Glass (no headspace)	Refrigerate, 4°C	14 Days
Semivolatile Organics	100	Glass	Freeze, -18°C Refrigerate, 4°C	1 Year[c] 14 Days[c]
Organotins	100	Glass	Freeze, -18°C Refrigerate, 4°C	1 Year[c] 14 Days[c]
Methyl Mercury	100	Teflon™ or Glass	Freeze, -18°C	28 Days
Mercury	50	Polyethylene, Glass (LDPE) or Teflon™	Freeze, -18°C Refrigerate, 4°C	28 Days[d] 28 Days
Metals	50	Polyethylene (LDPE)	Freeze, -18°C Refrigerate, 4°C	2 Years 6 Months
Microbiology	100	HDPE (Autoclaved)	Refrigerate, 4°C	24 Hours
Bioassay	7 Liters	Glass or Polyethylene	Refrigerate Protect from light	2 Weeks

Notes:

a. Minimum field sample size for one laboratory analysis. If additional QC analyses are required, the field sample size should be adjusted accordingly.
b. Sandier sediments require larger sample sizes than do muddier sediments.
c. Holding time to extraction. After extraction, holding time is 40 days to analysis.
d. A number of unpublished studies have demonstrated that freezing sediment samples may extend the holding time for mercury analysis up to 6 months.

3.7 Field Quality Control (QC)

Collection of one or more field QC samples may be required during a sediment sampling effort. The type and frequency of QC sample collection will be specified during the project planning process. A list of the various types of sediment QC samples follows:

3.7.1 Container Blank

A container blank is prepared at the analytical laboratory by filling one of the project's sample containers with analyte-free water or organic solvent. The blank is retained at the laboratory and analyzed along with samples collected in the same batch of containers. Container blank results are used to evaluate any contamination present in the sample containers.

3.7.2 Field Blank

A field blank is a sample of analyte-free water that is supplied by the laboratory. The field blank is generated by opening the analyte-free water container at the sampling location and transferring an aliquot to another laboratory-supplied container. The field blank may be analyzed for any or all of the analytes for which associated samples are being analyzed. Field blank results are used to measure and document any possible on-site contamination.

3.7.3 Preservation Blank

A preservation blank is a sample of analyte-free water that contains the same preservative used for associated samples and is analyzed for the same parameters. Analysis of the preservation blank is used to measure and document any contamination present in the preservative.

3.7.4 Rinsate (Equipment) Blank

A rinsate blank is a sample of analyte-free water that has been used to rinse sampling equipment after prescribed decontamination. The analyte-free water is supplied by the laboratory. The rinsate blank may be analyzed for any or all of the analytes for which the samples are being analyzed. Analysis of the rinsate blank is used to measure and document the effectiveness of field decontamination of sampling equipment and possible carry-over of contamination to samples collected after the rinsate blank.

3.7.5 Trip Blank

A trip blank is a sample of analyte-free water plus preservative that is prepared by the laboratory in a 40-ml volatile organic analysis (VOA) vial. It is transported to the sampling location, remains unopened during sampling, and accompanies the samples back to the laboratory. A trip blank is submitted only when sample analysis includes volatile organic compounds or gasoline. Analysis of the trip blank is used to indicate sample contamination during transport, or from bottle or sample storage, both before and after sampling.

3.7.6 Temperature Blank

A temperature blank is a plastic container of water that is kept in the sample cooler with analytical samples between sample collection and delivery. The temperature of this water is measured and recorded when samples are received at the analytical laboratory. Measurement of the temperature blank is used to indicate whether proper sample temperature was maintained between sample collection and delivery to the analytical laboratory.

3.7.7 Field Split Sample

A field split sample consists of an actual sample for which twice as much volume as necessary to fill the sample containers has been collected. Aliquots of this sample are equally distributed in two sets of sample containers. This division results in two (theoretically) equivalent samples collected from one sampling location. The field split sample is generally analyzed for the same set of analytes for which the original sample is being analyzed. Analysis of a field split sample may be performed by a second analytical laboratory; it is used to measure and document repeatability of sample handling procedures, heterogeneity of the sample matrix, and the standardization of analytical procedures.

3.7.8 Field Replicate

A field replicate consists of a second sample that is collected using the same sampling methodology used to obtain the first sample. It is collected at the same sampling location and as soon after the original sample as possible. The field replicate is generally analyzed for the same set of analytes as the original sample. Analysis of the field replicate is used to measure and document the repeatability of field sampling methodologies as well as the heterogeneity of the sample matrix. Any number of field replicates may be collected at a particular sampling location. Statistical analysis of numerical analytical results (mean and standard deviation) of the original sample and multiple replicates may also be performed to calculate the likely range of analyte concentrations at a given sampling location.

3.7.9 Background/Reference Sample

A background sample is collected from an area outside, but near to, the area of suspected contamination. It should be collected using the same sampling methodology during the same time period as the other samples. The background sample may be analyzed for any or all of the chemical analytes as the regular samples. Analysis of the background sample is used to measure background concentrations of analytes of interest in the general sampling area. A background sample collected for the purpose of bioassay testing is generally referred to as a *reference* sample.

3.8 Field Analyses

Several physical and chemical sediment parameters are best measured in the field because of the unstable nature of the parameter, or because the information is needed to direct further sampling. Four sediment field parameter measurements are described in this section.

3.8.1 Percent Fines

This procedure provides a gross field measurement of percent fines in a sediment sample. This field measurement is not intended to take the place of Particle Size Distribution analysis in the laboratory, but to aid in directing collection of bioassay samples and reference samples which can be dependent upon percent fines. Equipment required to perform this field measurement includes:

- USA Standard Testing Sieve #230 (63 µm opening),
- 50-mL measuring cup,
- 100-mL graduated cylinder,
- small plastic funnel,
- teaspoon,
- squirt bottle filled with water, and
- safety glasses or goggles and chemical-resistant gloves (if contamination is suspected to be present).

Once a sediment sample has been collected, the following procedures should be carried out.

- Thoroughly rinse the sieve and all other equipment and visually inspect to ensure that no sediment or other detritus is present.
- Collect a sediment aliquot from the grab sampler in the 50-mL cup, ensuring that exactly 50 mL is collected by "shaving" excess sediment from the top of the cup and rinsing any sediment off the sides of the cup.
- Transfer the sediment aliquot from the 50-mL cup to the sieve using the spoon. Thoroughly rinse the cup and the spoon into the sieve with water to ensure that the entire aliquot has been transferred.
- Gently rinse the sieve with running water and observe the stream of water coming from the bottom of the sieve. During this step, the fines are being rinsed away. Rinse until the stream of water appears clear. This indicates that all ***fines*** have passed through the sieve. Gently rinse the remaining sediment to one side of the sieve.
- Place the plastic funnel into the 100 mL graduated cylinder and position the lip of the sieve over the funnel. Using the squirt bottle, rinse the sediment into the graduated cylinder, directing the stream of water through the back of the sieve. Continue rinsing until all sediment has been transferred to the graduated cylinder. If needed, rinse any sediment that may have adhered to the funnel. The rinse water should not overflow the graduated cylinder. If it appears that the graduated cylinder will overflow before all sediment has been transferred, discard the sample and repeat the entire procedure.
- Allow the sediment to settle completely in the graduated cylinder and record the amount of sediment present. This measurement represents the ***volume retained***. Also record any turbidity observed in the overlying water.

The ***volume retained*** (in mL), subtracted from the original 50-mL aliquot, provides the volume that passed through the sieve, or ***volume of fines*** in 50 mL of sample. Multiplying this remainder by two gives the volume of fines in 100 mL or ***percent fines***. The formula can be stated as:

Percent fines = **(50 mL - Volume Retained in mL) x 2**

3.8.2 pH

Sediment pH may be measured by two methods, depending on the type of pH probe that is used. When using either method, it is important to calibrate the pH meter prior to field use. The meter should be calibrated according to manufacturer’s specifications with at least two buffers that will bracket the expected pH of the sediment samples. If the pH of a sediment sample falls outside the bracket of buffers in the initial calibration, the meter should be recalibrated with the proper buffers.

Sediment pH may be measured with a standard combination pH electrode by inserting the electrode directly into the sediment sample to a depth of approximately 2 centimeters. The measurement should be recorded after the reading has stabilized. It should be noted that this method can be extremely hard on sensitive combination pH electrodes and care should be taken when inserting the electrode. An alternate method is described below.

A “soil” pH electrode contains a concentric ceramic junction above the reference contact. Sediment pH may be measured with this type of electrode as follows.

- Collect approximately 5 grams of sediment from the sample and place the aliquot in a small container such as a test tube.
- Add approximately 5 milliliters of distilled water and mix completely.
- Allow the mixture to settle for approximately 15 minutes.
- Insert the pH electrode into the container so that the pH-sensitive bulb is immersed in the opaque sediment suspension and the reference contact remains in the relatively clear supernatent layer.
- Record the measurement after the reading has stabilized.

Whichever pH electrode is used, rinse the electrode in distilled water after each use and store it in buffer between measurements.

3.8.3 Redox Potential

Redox potential (or Eh) should be measured as soon as possible after sample collection due to the unstable nature of this parameter. Redox potential may be measured using a platinum electrode and combination pH/millivolt meter. The electrode is inserted directly into the sediment sample to a depth of approximately 2 centimeters. Record the measurement after the reading has stabilized.

The redox electrode should be calibrated prior to use with a solution of potassium ferrocyanide and potassium ferricyanide. Manufacturer’s directions for preparation of the calibration solution are included with the electrode. This solution is poisonous and should be labeled, stored and handled accordingly. Most electrodes should calibrate to a value near +192 millivolts using this calibration solution.

3.8.4 Interstitial Salinity

The salinity of pore or *interstitial* water contained in a sediment sample may measured directly in the field. An aliquot of the sediment sample is placed in a separate container not intended for chemical analysis and the sediment solids allowed to settle. The salinity of the overlying interstitial water may be measured directly using a salinometer. The salinometer should be calibrated prior to use according to manufacturers directions with a salinity standard of a concentration (in parts per thousand) close to that expected in the field. If the salinometer has a temperature compensation feature, the temperature of the interstitial water should be measured prior to the salinity measurement and the salinometer adjusted accordingly.

Salinity of the interstitial water may also be measured indirectly with a conductivity meter. The meter should be calibrated prior to use with a known conductivity standard (in umhos/cm or uS/s) close to the conductivity expected at the sampling site and temperature measured prior to the conductivity measurement. Conductivity and temperature measurements may be used to calculate salinity according to methods outlined in Standard Method (SM) 2520B (APHA, 1985).

4. SAMPLING PROCEDURES FOR MARINE WATER

This section describes sampling procedures for the collection of marine water column samples for analysis of conventionals, metals, organic, and microbiological parameters.

4.1 Sampler Types and Operation

As mentioned in Section 2.4.2, the typical water bottle sampler consists of a cylindrical tube with stoppers at each end, and a closing device that is activated from the surface by a messenger or an electrical signal. Multiple water samplers can be attached sequentially to a vertical hydrowire for sampling at multiple depths on a single cast, or they can be mounted on a rosette frame (often in conjunction with an *in situ* sensor array) which allows for collection of replicate samples at the same depth.

During deployment, the stoppers at both ends of the sampler are cocked open and the air vent and drain are closed. If any of the bottles carry reversing thermometers, the holders should be flipped into the cocked position. It is critical that the stoppers and interior of the sampler remain free from contamination. All members of the sampling team should avoid touching the stoppers and the insides of the sampler.

Reversing thermometers must be treated carefully. This type of thermometer must always be carried and stored in the vertical position, never horizontal. During long-term storage, the thermometer should be stored with the mercury reservoir at the bottom. When not in use, the thermometer should be 'exercised' two or three times by hand-flipping it end-to-end (moving quickly through the horizontal plane without pause). All reversing thermometers should be checked and documented for calibration at a certified calibration facility once a year.

After the sampler is cocked, it is lowered to a designated depth. Avoid deploying water bottles in obvious surface slicks as these can contaminate samples with organic compounds, etc. Be aware that not all surface microlayer contamination will be in the form of visible slicks. If contamination by the surface microlayer is of concern, use samplers that are designed to remain closed until they have descended below the microlayer (e.g., Go-Flo™ bottle from General Oceanics, Inc., Miami, Florida). Teflon™-lined Go-Flo™ bottles are recommended when sampling marine water that will be analyzed for ambient or trace levels of mercury.

Once the sampler reaches the desired depth, it should be allowed to equilibrate to ambient conditions for approximately 1 minute before it is closed. If reversing thermometers are involved, equilibration should be 5 minutes. Note that a pair of unprotected reversing thermometers is adequate for the waters of Puget Sound; the depths encountered are not sufficient to create an appreciable pressure differential offset between unprotected and protected instruments. After equilibration, the closing device is activated by a messenger or electrical signal, and the sampler is retrieved. When deploying a mechanical messenger, an attempt should be made to maintain a minimum wire angle. Extreme wire angles, if unavoidable, should be recorded in field notes. To ensure that all samples are truly representative of the water column within a specific water parcel, it is advisable that they be collected from a single cast. Multiple casts cannot meet this objective, as ambient conditions change too rapidly near the surface. If sampler failure occurs at depth, it may be acceptable to deploy another single cast at this depth since conditions show much less variation over time.

As the water samplers are being brought on board, each bottle should be checked immediately for leakage of sample water around the seals; there should be no sample loss from any orifice. A visual inspection is usually sufficient, as the weight of the water with the bottle suspended in air will force its way around a weak seal. If the sample has been compromised, the cast should be repeated.

4.2 Sample Collection and Preservation for Specific Parameters

The following sections describe sample collection procedures unique to conventionals, metals, organics, and microbiological analytical parameters. Recommended sample volumes, containers, preservation techniques, and holding times for water samples are summarized in Table 3.

4.2.1 Conventionals

Acceptable water samples should be subsampled as soon as possible (i.e., within 15 minutes), as appreciable delay may result in unrepresentative subsamples. For example, measurement of variables sensitive to biological alteration (e.g., dissolved oxygen, color, nutrients, etc.), or settlement within the water sampler (e.g., suspended/settleable solids, turbidity, phytoplankton, etc.) can be biased substantially by subsampling delays. Dissolved oxygen should be the first parameter collected, followed in order of priority by those parameters which would be the most affected by subsampling delays. It may be allowable to gently invert the sampling bottles end-over-end to homogenize the contents, but only after the dissolved oxygen sample aliquots have first been collected.

4.2.2 Metals

The recommended method for metals sample preservation depends on the type of analysis that will be conducted. Samples that will be analyzed for total metals or total mercury should be acidified to $pH<2$ using ultrapure HNO_3. Samples that will be analyzed for mercury speciation should be preserved with HCl rather than HNO_3. Samples that will be analyzed for both dissolved and particulate metals should be filtered as soon as possible, within 24 hours of collection is advisable. The filtrate, which contains the dissolved fraction, should be preserved by acidifying to $pH<2$ using ultrapure HNO_3. The particulate fraction, which is retained on the filter, is frozen for preservation.

Marine and estuarine water samples have high ionic strength resulting in a buffering capacity that impacts the amount of acid required for preservation. The pH of these samples should be confirmed and documented to be less than 2 at the time of preservation by pouring off a small amount of sample and checking it with short range pH paper. Excess acid should be avoided because preconcentration techniques for some metals analyses are strongly dependent on pH. Suggested final concentration of the HNO_3 in the sample is 0.15 percent but the pH should be checked carefully to ensure proper preservation of the sample. Additional information on the preservation of marine water samples may be found in Section 4 of PSEP, 1997b.

Studies of metals in the water column may require separation of dissolved and particulate fractions, depending on project objectives. For the purposes of the PSP&G protocols, the particulate fraction of a water sample is defined as the material that is retained on a 0.4- or 0.45-µm filter. Several of the most commonly used filters have a nominal pore size of 0.4 µm. The dissolved fraction consists of the material in the filtrate (i.e. the material that passes through the 0.4- or 0.45-µm filter). Additional information on collection of dissolved and particulate samples is available in PSEP, 1997b and *Recommended*

Guidelines for Measuring Conventional Water Quality Variables and Metals in Fresh Water of the Puget Sound Region (PSEP, 1990). Any device used to separate particulate material from water samples may contribute contaminants to the sample taken for analysis. This contamination must be determined in advance and reduced whenever possible.

Filtration is preferable to other techniques for many analyses because the required equipment is relatively inexpensive (i.e., a high speed centrifuge is not required), and filtration provides a sample that is suitable for direct chemical analysis (i.e., an extractable or digestible residue on a filter). The amount of particulate material that may be collected on a filter (typically less than 10 mg) may limit this technique for low-level metals analyses. Centrifugation techniques can yield comparable results and may be used to collect larger amounts of particulate material (e.g., several grams). Use of centrifugation requires careful and complete transfer of the sample from the centrifuge prior to analysis.

Horowitz (1986) describes a fixed-angle head or swing-bucket rotor centrifugation technique for metals analysis in large-scale studies (e.g., 2,000 to 3,000 samples per year). Bates, et al., (1983) describe a continuous-flow centrifugation technique (using a Sorvall Model SS-3 or RC-5 high-speed centrifuge) for collection of particulate material for hydrocarbon analyses. Bates, et al., (1983) noted that continuous-flow centrifugation may not recover fine-grained particles in the 1 to 2 µm range as efficiently as filtration. Because these very small particles may have a higher loading of metals than larger particles, continuous-flow centrifugation may not quantitatively recover the metals in the particulate phase of a water sample.

A detailed protocol for shipboard filtration of large volumes of sea water using commercially available equipment is given by Mart (1979). A completely submersible, self-contained, filtration apparatus, capable of filtering up to 1,000 L at a flow rate of 50 to 200 mL/min, is commercially available from Seastar Instruments, Ltd., Sidney, British Columbia, Canada. Clean conditions, are essential for filtering sea water. If field conditions cannot be adequately controlled, then filtering should be conducted in a laboratory environment. However, filtration and preservation must occur within 24 hours of sample collection.

Sections 5.3.1 and 5.3.2 of the Metals chapter (PSEP, 1997b) describe laboratory methods for dissolved and particulate metals sample preparation. Additional information about water column samples collected for the analysis of ultratrace level metals can be found in EPA Method 1669 *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (EPA, 1995).

4.2.3 Organics

Although collection of water column samples for organics analyses is not common in the four major Puget Sound programs, the following basic guidelines are included.

- Collect samples for the analysis of volatile organic compounds first. Samples should be collected in 40 ml VOA vials leaving no head space.
- Protect samples from possible contamination such as fuels, winch grease, exhaust, and solvents that may be present on or around a research vessel.

Preserve water samples collected for organics analysis as soon as possible, according to the guidelines summarized in Table 3.

4.2.4 Microbiology

Water sampling can result in highly variable data because bacteria are not uniformly distributed throughout the water column (Gameson, 1983) and sample volumes generally are limited to 50 to 100 ml. One major cause of spatial heterogeneity is the tendency for bacterial cells to concentrate in a thin microlayer on the surface of the water. Because bacterial abundances in the microlayer may exceed abundances in underlying surface water by several orders of magnitude (Hardy, 1982), it is recommended that the microlayer and underlying water be sampled separately. However, sampling of the microlayer requires specialized techniques that have yet to be standardized. Also, collection and analysis of samples from both the microlayer and underlying water at each station may be too expensive for many routine monitoring programs. Thus, if separate samples cannot be collected within the constraints of a particular program, it is recommended that the microlayer be included in the sample by using the traditional "scoop" method of surface water sampling (EPA, 1978). This method involves plunging an open bottle straight down to a depth of 15 to 30 cm below the water surface, moving it horizontal to the surface while tipping it slightly to let trapped air escape, and removing the bottle in a vertical position. Approximately 2.5 cm of headspace is required in the sample container. Sample containers should be isolated from contact with wet ice as it could impart contamination to the sample.

4.3 Field QC

Collection of one or more field QC samples may be required during a water column sampling effort. The type and frequency of QC sample collection should be specified during the project planning process. The field QC samples described in Section 3.7 apply to water column sampling as well as sediment.

Table 3
Recommended Sample Sizes, Containers, Preservation Techniques, and Holding Times for Water

Parameter	Minimum Sample Size (ml)[a]	Container	Preservation Technique	Holding Time
Alkalinity	100	Glass or Polyethylene	Refrigerate, 4°C	14 Days
Total Hardness	100	Glass or Polyethylene	Refrigerate, 4°C HNO_3 to pH<2	6 Months
Total Phosphorous	50	Glass or Polyethylene	Refrigerate, 4°C H_2SO_4 to pH<2	28 Days
Orthophosphate	50	Glass or Polyethylene	Refrigerate, 4°C[g] Filter on Site	48 Hours
pH	25	Glass or Polyethylene	None	Analyze Immediately[b]
Salinity	200	Glass or Polyethylene	None	28 Days
Turbidity	100	Glass or Polyethylene	Refrigerate, 4°C	48 Hours
Total Suspended Solids	1,000 to 4,000[d]	Glass or Polyethylene	Refrigerate, 4°C	7 Days
Dissolved Oxygen Winkler	125	Glass Bottle with Glass Top	Fix with $MnCl_2$ and Alk. Iod. (2 ml ea.)	8 Hours (store in the dark)
Dissolved Oxygen Probe	125	Glass Bottle with Glass Top	None	Analyze Immediately[b]
Ammonia - N	100	Glass or Polyethylene	Refrigerate, 4°C H_2S0_4 to pH < 2[g]	28 Days
Nitrite - N	100	Glass or Polyethylene	Refrigerate, 4°C[g]	48 Hours
Nitrate - N	100	Glass or Polyethylene	Refrigerate, 4°C[g]	48 Hours
Silica	100	Polyethylene	Refrigerate, 4°C[g]	28 Days
Chlorophyll a	25 to 1,000[d]	Glass or Polyethylene (Dark)	Store filters frozen (-20°C) in the dark[f]	28 Days[f]

(cont. on next page)

Table 3 (Continued)

Parameter	**Minimum Sample Size (ml)**[a]	**Container**	**Preservation Technique**	**Holding Time**
Volatile Organics	80	Glass -2 40 ml vials No Headspace	Refrigerate, 4°C HCl to pH<2	14 Days
Semivolatile Organics	1,000 to 2,000	Glass	Refrigerate, 4°C	7 Days[e]
Total Mercury and Diss. Mercury	500	Teflon™ or Glass with Teflon™ Cap	Refrigerate, 4°C, HNO_3 to pH<2[g,h]	28 Days
Total Metals and Diss. Metals	1,000	Polyethylene or Teflon™	Refrigerate, 4°C, HNO_3 to pH<2[g]	6 Months
Microbiology	500	HDPE (Autoclaved)	Refrigerate, 4°C	24 Hours

a. Minimum field sample size for one laboratory analysis. If additional QC analyses are required, the field sample size should be adjusted accordingly.
b. Immediately means as soon as possible after the sample is collected, generally within 15 minutes. These parameters should, ideally, be measured in the field.
c. After filtration.
d. The volumes specified are only estimates; the actual volume collected and filtered depends on concentration and analytical methodology used and may be larger than those presented in the Table.
e. Holding time to extraction. After extraction, holding time is 40 days to analysis.
f. Samples collected for the analysis of chlorophyll *a* must be kept cold until sample filtration. Filtration should occur as soon as possible after sampling. The filter may be immersed in 90 percent acetone solution and frozen which may significantly extend the holding time, however, this method is not approved for use on projects that come under regulatory scrutinity. Prolonged exposure of the filter to air can result is a loss of chlorophyll *a*.
g. Samples for analysis of total mercury and total metals should be preserved within 24 hours of sample collection, preferably in the field immediately following sample collection. Samples for analysis of dissolved mercury and dissolved metals must be preserved after filtration. Filtration and/or preservation of metals samples and the nutrients orthophosphate, ammonia nitrogen, nitrate, nitrite, and silica must occur within 24 hours of sample collection, preferably in the field immediately following sample collection. Holding times for nutrient samples may be extended up to 60 days by freezing but this methodology may not be allowed if samples are collected under certain regulatory programs.
h. Samples collected for analysis of very low levels of mercury or for mercury speciation should be preserved with HCl rather than HNO_3.

Footnote: When it is not feasible to preserve metals samples in the field, preservation must as soon as possible. Metals samples not preserved within 24 hours must sit at least 16 hours after preservation before analysis begins. Metals samples should always be filtered within 24 hours of collection.

4.4 *In situ* Measurements

There is a wide variety of instruments that are capable of measuring water column variables *in situ*. Most are deployed from the sampling vessel using a hydrographic wire or conducting cable. These submersible sensor arrays measure the variables of interest and either transmit electronic data to recorders on the survey vessel, or store the data on a logger within the submersible package. The earliest sensing instruments were designed as CTD (conductivity/temperature/depth) systems to measure conductivity (for conversion to salinity and in calculation of density), water pressure (for conversion to depth) and temperature. Additional sensors can be included to measure other water column variables such as dissolved oxygen, pH, irradiance, turbidity, oxidation-reduction potential and chlorophyll *a*.

There are significant advantages when taking *in situ* water column measurements, such as:

- data on selected variables can be collected in real time, and
- continuous depth profiles are possible (to characterize water structure).

4.4.1 Equipment Acquisition

When selecting the type of in situ instrument for use in marine and estuarine waters, the following factors should be considered:

- the research vessel might have equipment handling limitations such as deck space or lifting capacity;
- the system should be capable of operating within the prescribed ranges for accuracy and precision, as specified by the project plan;
- the system should have good electronic stability and be relatively immune to external electrical interference;
- the system should be easy to calibrate on board the survey vessel;
- the cable should meet expected work load requirements and be easily repaired;
- automatic data logging should occur only under increasing depth increments to avoid data pile up;
- data uploading capabilities should be compatible with database software and hardware; and
- the vendor should be able to supply good service support.

4.4.2 Equipment Calibration

Typically, the accompanying operating manuals should provide detailed descriptions of equipment calibration, operation and maintenance. The manufacturer should also be able to provide specific guidance if necessary. Instruments should be calibrated at a certified calibration lab annually; full documentation should be provided. An annual or semiannual intercalibration effort among the various groups that measure water-column variables in Puget Sound could be useful for ensuring data comparability and quality. When attainable, National Institute of Standards and Technology (NIST) or other similar data traceability is encouraged.

Usually, the higher the degree of probe resolution and precision, the more expensive the instrument. This is because more sophisticated devices have features such as greater noise filtration capabilities, more stable power supplies, faster processors, and better cushioning/mounting of internal components. For example, an instrument with a precision of +/- 0.05 for conductivity and temperature may cost less than $10,000, whereas another model with specifications of +/- 0.005 may be $50,000. It is important to remember that instrument specifications, as stated in the manual, will reflect hypothetical probe performance at the lab bench onshore; performance while at sea under adverse conditions will usually not be as good.

The following general criteria should be considered during instrument calibration:

- the instrument should be allowed to warm up prior to calibration as specified in the manual;
- sensors should be field-calibrated according to manual instructions at the beginning and end of each sampling day;
- if instrument stability is suspect, sensor calibration should be checked immediately before redeploying; and
- routine maintenance and inspection of *in situ* instruments should follow the manufacturer's recommendations, and detailed records of all maintenance activities should be kept for quality assurance purposes.

Discrete water samples should always be collected simultaneously with respective sensor measurements to establish sensor offsets for later data correction. Typically, calibration samples are collected at the top and bottom of the water column for each cast, or at several discrete depths on a cast at the beginning and end of each sampling day. *In situ* fluorescence and dissolved oxygen sensors should be checked against several profiles rather than only one or two discrete samples.

4.4.3 Equipment Operation

Although instrument operating manuals should be consulted for specific instructions, the following general procedures for operating *in situ* instruments have a direct influence on data quality and apply for most models.

- The sealing parts of all underwater connectors and housings should be cleaned and lightly coated with silicone grease to ensure proper lubrication and watertight integrity.
- Cables should be inspected for nicks, cuts, abrasions, or other signs of physical damage, and repaired as needed, prior to submersion (a flooded cable is usually irreparable).
- Desiccant should be inspected and replaced when necessary.
- Battery condition should be checked periodically.
- Sensors should be housed in such a way as to provide protection from direct impact, yet still allow for unrestricted exposure to water flow around the sensor heads.
- Optical surfaces should be cleaned with a detergent solution, rinsed with fresh or distilled water, and dried with lens tissues prior to deployment.
- During deployment, the survey vessel should attempt to maintain position. The degree of vessel motion and sea state should be noted if data results are thought to be adversely influenced.
- The sensors should be deployed from a part of the vessel that is outside the immediate influence of prop wash and possible vessel contaminants (e.g., bilge and head discharges, oil/fuel slicks, etc.).
- If possible when measuring continuous profiles, the descent rate should not exceed the equilibration rate of the sensor having the slowest response time (electro-chemical probes will always have a slower response than electronic sensors).
- Cable strain should not exceed recommended working load, nor should the specified bend radius be reduced while under a load.
- Sensors and associated sampling bottles should be rinsed with fresh water after each sampling event.

- External sensors and optical ports should be covered for protection when not in use for any length of time (this will vary based on probe type).
- Instruments should be safely secured when on deck, and preferably stored in shipping boxes when not in use.

To facilitate shipboard repair of *in situ* instruments, it is recommended that critical spare parts be stored on the sampling vessel. Factory inspection and recalibration at recommended intervals are essential to ensure that the *in situ* instruments will continue to function properly during operational cruises. It is strongly recommended that factory service be conducted at least once a year. Factory service may also be required when part of an *in situ* system is replaced, as not all components are necessarily interchangeable without factory recalibration.

4.5 Field Analyses

Physical and chemical water analyses that may be performed in the field as well as in the analytical laboratory include:

- pH,
- conductivity,
- dissolved oxygen,
- turbidity, and
- salinity.

It is frequently preferable to perform these analyses in the field, especially if the samples will not be immediately transported to the analytical laboratory (pH, in particular, should be measured in the field if feasible). In addition, measurements of temperature and transparency can only be collected accurately in the field.

4.5.1 Temperature

Water temperature may be measured with an alcohol, mercury or digital thermometer. Temperature should be measured as soon as the sample is collected to obtain a measurement that is an accurate representation of the *in situ* sample temperature. If possible, it is recommended that alcohol or digital thermometers be used in place of mercury thermometers to avoid possible breakage and introduction of mercury into the environment and to remove a source of possible contamination to samples collected for the analysis of mercury. All instruments used to measure temperature should be traceable to a NIST temperature reference.

4.5.2 Transparency

Water column transparency is measured with a Secchi disk. A Secchi disk is a weighted, black and white or all white disk lowered into the water body on a calibrated rope or line. The disk is lowered until it is just visible to the sampler and the depth, as measured from the water surface, is recorded in feet or meters. The all-white disk may be preferable when the water transparency is high. Either disk, however, is acceptable to use.

4.5.3 pH

The pH of a water column sample may be measured in the field using a pH meter. The meter should be calibrated according to manufacturers' specifications with at least two standards of known pH. The pH of these standards should bracket the expected pH at the sampling site. For example, if the pH at the sampling site is expected to be basic (pH 7 to 14), standards of pH 7.00 and 10.00 should be used to calibrate the meter. If pH measurements at the sampling site do not fall within the initial calibration range, the meter should be recalibrated with appropriate standards and sample pH remeasured for those samples which fell outside the calibration range.

4.5.4 Dissolved Oxygen

Dissolved oxygen may be measured in the field by either a dissolved oxygen meter and probe or by a field-portable Winkler titration kit. If using a meter and probe, the system should be calibrated prior to use with a zero oxygen standard and a second standard of known oxygen content. The second standard should be checked by performing a Winkler titration. When measuring dissolved oxygen with a meter and probe, the sample should be swirled or stirred constantly until the reading stabilizes and the measurement is recorded.

4.5.5 Turbidity

Turbidity may be measured in the field with a field-portable nephelometer (turbidity meter). The meter should be calibrated prior to use with at least two standards of different but known turbidity (in nephelometric turbidity units or NTUs). The two standards should attempt to bracket the range of turbidity measurements expected at the sampling site. When performing field analysis for turbidity, samples should be analyzed as soon as possible after collection. If immediate analysis is not possible, the sample should be agitated prior to analysis to resuspend any settled solid material.

4.5.6 Salinity

Salinity may be measured in the field with a salinometer. The meter should be calibrated prior to use according to manufacturer's directions using a standard of known salinity (in parts per thousand). The salinity of the standard should be close to the expected salinity of the sampling site. When measuring a sample for salinity, the sample should be swirled or stirred until the meter stabilizes and a measurement is recorded. Salinity may also be calculated from the measured conductivity and temperature of a sample. The conductivity is measured with a conductivity meter that has been calibrated according to manufacturer's directions to known conductivity standards (in umhos/cm or uS/s). Salinity is calculated from the conductivity and temperature according to Standard Method 2520B (APHA, 1985). Gross salinity measurements may also be taken with a field-portable refractometer. This instrument will provide salinity measurements with an accuracy of 1 to 2 parts per thousand.

5. SAMPLING PROCEDURES FOR TISSUE

This section is concerned with various issues relating to the collection of biological tissue samples for the analysis of metal, organic and microbiological parameters.

5.1 Sample Collection

The methods used to obtain tissue specimens will vary, based upon the species of interest, since most marine taxonomic groups are habitat specific. For example, it is usually most practical to collect salmon and other pelagic (free-swimming) species through the use of some type of commercial fishing gear. One common problem with pelagic species is that, due to their mobility, it is hard to determine if the individuals collected are truly representative of the population within a given locale. (Purchasing specimens at a dock or a store is usually not recommended, as point-of-origin records are not reliable.) Field records should include the type of collection equipment used, the size of the area covered, geographical references, etc.

Shellfish and other intertidal taxa can be hand-collected on a favorable tide. Only intact specimens should be retained for analysis (the tightly-closed shell, or carapace, makes an excellent barrier between the internal tissues and the outside environment). For studies involving human health risk assessment, it is recommended that specimens be collected by the same methods as those used by the people whose health risk is being assessed. Recommended sample sizes, containers, preservation techniques and holding times are summarized in Table 4.

A primary concern is to avoid contaminating tissue specimens during collection and transportation to the analytical lab. In the field, contaminating agents may be in the form of cross-contamination from sampling gear, shipboard lubricants, engine exhaust, atmospheric particles or meltwater from ice used for cooling. Efforts should be made to minimize sample handling and to avoid sources of contamination. One way to avoid contamination is to wrap whole samples (e.g., mollusks in shell, whole fish) in aluminum foil (dull side in) and place in watertight plastic bags in a covered ice chest, with ice. The aluminum foil may be precleaned with acetone or heat-treated prior to use if low-level trace organic analyses are to be performed. If low-level trace metals analysis (especially of aluminum) will be performed on the tissue sample, it is recommended that an alternative to aluminum foil be considered such as pre-cleaned polypropylene or Teflon™ sheets.

Sources of contamination may also be avoided by resecting (i.e., surgically removing) tissue in a controlled environment. Organisms should not be frozen prior to resection if internal organs are included in the analysis, as freezing may cause some internal organs to rupture and contaminate other tissues. If organisms are eviscerated on board the survey vessel, the remaining tissue may be wrapped as previously described and frozen.

5.2 Field QC

Field QC procedures for tissue sampling and processing are limited to minimization of contamination described in previous and following sections. Field QC samples collected as a check for contamination may include equipment and container blanks. Field replicate samples are generally specified in the project planning document and may be included as a check of sample variability rather than a check of sampling methodology.

5.3 Sample Processing

Tissue resection and any subsampling of specimens should be conducted in a dust free environment. In most cases, this requires that organisms be transported on ice to a laboratory, rather than being resected on board the sampling vessel. Resection must be conducted by or under the supervision of a knowledgeable biologist. For fish samples, special care must be taken to avoid contaminating target tissues (especially muscle) with slime and sediment from the fish skin during resection. The incision troughs are subject to such contamination and should not be included in the sample. In the case of muscle, a core of tissue is taken from within the area bordered by the incision troughs, without contacting them.

5.4 Special Considerations

Sections 5.4.1 through 5.4.3 describe special sampling and processing considerations for tissues undergoing metal, organic, or microbiological analyses.

5.4.1 Metals

Resection is best performed under "cleanroom" conditions. The cleanroom should have positive pressure and filtered air. It should also be isolated from highly contaminated samples (e.g., containing hazardous waste). At a minimum, care should be taken to avoid contamination from dust, instruments, and all materials that may come in contact with the samples. If gloves are worn during resection, they must be powder-free.

The best equipment to use on tissue samples intended for trace metal analyses is made of quartz, polypropylene, polyethylene or fluoropolymers. Stainless steel that is resistant to corrosion may be used if necessary. Corrosion resistant stainless steel is not magnetic, and thus can be distinguished from other stainless steel by applying a magnet. Stainless steel scalpels have been found not to contaminate mussel samples (Stephenson, et al., 1979). However, other biological tissues (e.g., fish muscle) may be contaminated by exposure to stainless steel. Quartz utensils are ideal but expensive. Titanium knives may be used and can be made inexpensively from titanium sheet metal. Titanium, however, is soft and the knives may be difficult to keep sharp. Ceramic knives have been used successfully for tissue cutting. To minimize contamination when resecting tissue, separate sets of utensils should be used for removing outer tissue vs. removing tissue intended for analysis.

Sample size requirements can vary with tissue type and detection limit requirements. In general, a minimum sample size of 6 grams (wet weight) is required for a single analysis of all priority pollutant metals. A separate sample of a least 5 grams (wet weight) is required for a single mercury analysis. Larger samples should be collected to allow for duplicates, spikes, and required reanalyses.

5.4.2 Organics

To avoid cross-contamination, all equipment used in sample handling should be thoroughly cleaned before each sample is processed. All instruments must be of a material that can be easily cleaned (e.g., stainless steel, anodized aluminum, borosilicate glass). Before the next sample is processed, instruments should be cleaned (e.g., washed with a detergent solution, rinsed with tap water, soaked in high-purity acetone or dichloromethane, and finally rinsed with analyte-free water). Work surfaces should be cleaned with 95 percent ethanol or other similar cleaning agent and allowed to dry completely.

The removal of biological tissues should be carried out by skilled persons that have been trained by an experienced biologist. Tissue should be removed with clean stainless steel or quartz instruments (except for external surfaces of the specimen). The specimens should come into contact with precleaned glass surfaces only. Polypropylene, polyethylene, and other plastic surfaces and implements are a potential source of contamination and should not be used. To control contamination when resecting tissue, separate sets of utensils should be used for removing outer tissue and for resecting tissue for analysis.

The tissue sample should be placed in a clean glass or PTFE container (e.g., containers that have been washed with detergent, rinsed at least once with tap water, rinsed at least twice with analyte-free water, rinsed with acetone, and, finally, rinsed with high-purity dichloromethane). Firing of the glass jar at 350°C for 4 hours may be substituted for the final solvent rinse only if precautions are taken to avoid contamination as the container is dried and cooled. Jars used to store samples intended for VOA should not be solvent rinsed but instead, should be heated to greater than 105°C as a final preparation step.

5.4.3 Microbiology

Shellfish sampling is very important because the consumption of shellfish, sometimes in the raw state, may present a serious public health hazard. Shellfish offer several advantages for sampling: they concentrate bacteria, can be sampled relatively easily and reflect pollution levels over relatively long periods in both sediment and water. In Puget Sound it is recommended that one or several shellfish species of recreational or commercial importance be sampled routinely at each major harvesting area. The use of a small number (preferably one) of species as standards will reduce the variation among stations and sampling periods that results from interspecies differences in the propensity to concentrate bacteria. Because of the variability of microbial concentrations in different types of tissues and species, the part of the organism selected for analysis should be based on project objectives, most likely driven by human consumption of specific tissue types. While the protective shell of most shellfish will preclude contamination from sampling implements, care should be taken not to introduce microbial contamination to the sample organisms. As soon as specimens have been collected, they should be placed into polyethylene bags with minimal handling by the sampling personnel. Recommended procedures for processing shellfish samples for microbiological analysis can be found in PSEP, 1986c. Processing of samples is best performed in a controlled environment such as the biology laboratory.

5.5 Sample Storage

Recommended sample storage conditions for metal, organic and microbiological analyses are summarized in Table 4. Resected tissues should be stored frozen at -18°C until analysis. Tissue samples intended for metals analysis should be stored in precleaned polyethylene or glass containers. Container lids must not have aluminum or cardboard liners. The recommended material for container lid liners is PTFE. Tissue samples intended for analysis of both metals and organic compounds can be stored in glass or fluoropolymer containers.

No holding time criteria for tissue samples are specified by EPA for metals analysis. Because mercury is volatile, the EPA holding time criterion for water samples intended for mercury analysis is 28 days. Previous Puget Sound Estuary Program (PSEP) workshop participants agreed that the 28-day maximum holding period is also appropriate for tissue samples intended for mercury analysis. Workshop participants further agreed to recommend a 2-year maximum holding time for tissue samples intended for analysis of metals other than mercury. In an unpublished study by the Washington Department of Fish and Wildlife and the King County Environmental Laboratory, fish muscle samples stored in glass containers and frozen at -20°C were analyzed for mercury before and after the 28-day holding time. Samples were analyzed at 6 different times, ranging from 4 to 86 days after sample collection. No significant differences in mercury concentrations were observed. Based on these results it is suggested that a frozen holding time of 3 to 6 months is acceptable for mercury in tissue and further study may be warranted.

Recommended holding times for frozen tissue samples have also not been established by EPA for organics analyses, but a 1-year maximum holding time (similar to the sediment holding time) is recommended for Puget Sound studies. Extracts should be analyzed within 40 days. Extended sample storage in a glass jar can minimize desiccation. At a minimum, the samples should be kept frozen at -18° C until extraction. This temperature will slow biological decomposition of the sample and decrease loss of moisture. Because of the potential rupture of tissue cells upon freezing, liquid associated with the sample when thawed must be maintained as part of the sample or extracted separately and combined with the tissue extract.

Table 4
Recommended Sample Sizes, Containers, Preservation Techniques, and Holding Times for Tissue

Parameter	Minimum and Recommended Sample Sizes (g)	Container	Preservation Technique	Holding Time
Metals	6[a] (50 recommended)	Polyethylene (LDPE) or Teflon™	Freeze[b], -18°C	2 Years
Mercury	5[a] (50 recommended)	Polyethylene, Glass (LDPE) or Teflon™	Freeze[b], -18°C	28 Days[d]
Semivolatile Organics	30[a] (100 recommended)	Glass or Teflon™	Freeze[b], -18°C	1 Year[c]
Volatile Organics	5[a] (20 recommended)	Glass or Teflon™	Freeze[b], -18°C	14 Days
Bacteriology	100	Plastic or Glass	Refrigerate, 4°C	24 Hours

Notes:

a. Weight is a minimum for a single analysis of resected, homogenized tissue. Studies using specific organs may require more tissue. Recommended sample size refers to the minimum amount of resected sample and accounts for tissue lost during homogenization.

b. Post-resection.

c. Holding time to extraction. After extraction, holding time is 40 days to analyze.

d. A number of unpublished studies have demonstrated that freezing tissue samples may increase the holding time for mercury analysis up to 6 months.

6. SAMPLE HANDLING

This section describes sample handling procedures that include sample shipment, chain of custody protocols and holding times and conditions.

6.1 Sample Shipment

All samples should be shipped or delivered to the analytical laboratory immediately after completion of sampling. This minimizes the number of people handling samples and protects sample quality and security. The following guidelines apply to water and sediment samples. Shipping protocols for tissue samples will most likely be project specific and should be stated in the project planning document. As samples are prepared for shipping, the following guidelines should be observed.

- Shipping containers should be in good shape and capable of withstanding rough treatment during shipping.
- Samples should be packed tightly with dividers separating all glass containers and empty space within shipping boxes filled so that jars are held securely.
- Sample coolers should be packed with ice to maintain an ambient sample temperature of approximately 4°C until delivery to the analytical laboratory. Either “water” ice or synthetic “blue” ice may be used in shipping. Both types of ice should be packaged in a manner that will preclude leaking inside the sample cooler. A temperature blank (see Section 3.7.6) may be placed in the sample cooler along with the analytical samples.
- All coolers must be leakproof. If a cooler is not leakproof by design, the interior should be lined with two heavy-duty plastic bags and the tops of bags should be tied once samples are inside. Adequate absorbent material should be placed in the container in a quantity sufficient to absorb all of the liquid.
- All samples should be accompanied by a sample analysis request. Parameters to be analyzed by the laboratory, and total number and kind of samples shipped for analysis should be listed on the request sheet. The laboratory should acknowledge receipt of shipment by signing and dating the form, and returning a copy to the designated project QA coordinator or sample manager.
- A chain of custody record for each shipping container should be filled out completely and signed. The sample analysis request and chain of custody record are frequently combined into one form. Chain of custody procedures are more fully described in Section 6.2.
- The original chain of custody record and analysis request should be protected from damage and placed inside the shipping box. A copy of each should be retained by the shipping party.
- A custody seal should be attached so that the shipping box cannot be opened without breaking the seal.
- For shipping containers carrying glass sample containers a "This End Up" label should be attached to each side to ensure that jars are transported in an upright position and a "Fragile-Glass" label should be attached to the top of box to minimize agitation of samples.
- Shipping containers should be sent by a carrier that will provide a delivery receipt. This will confirm that the contract laboratory received the samples and serve as a backup to the chain of custody record.
- Sample shipments by common carrier or air freight must be packaged and labeled according to U.S. Department of Transportation regulations or the International Air Transportation Association requirements. Packaging must account for suspected types and levels of contaminants in the samples as well as chemicals used to preserve the samples. The information may influence required packaging and labeling requirements. Failure to properly package and label sample shipments can subject the person offering the shipment to potential fines and legal action.

At the analytical laboratory, the sample custodian should oversee:

- receipt of samples;
- measurement and recording of the temperature blank;
- maintenance of chain of custody records;
- maintenance of sample tracking logs;
- distribution of samples for laboratory analyses;
- sending of samples to outside laboratories;
- supervision of labeling, log keeping and data transcription; and
- storage and security of all samples, data, and documents.

Upon receipt of samples, a designated laboratory custodian should fill out the chain of custody record, indicating time and date of reception, number of samples and condition of samples including sample size, container type and preservation. All irregularities indicating that sample security or quality may have been jeopardized (e.g., evidence of tampering, loose lids, cracked jars) should be noted on the sample analysis request form and returned to the client-designated QA coordinator. In addition, a sample manager or designated laboratory person should initiate and maintain the sample tracking log that will follow each sample through all stages of laboratory processing and analysis.

Minimum information in a chain of custody sample tracking log includes:

- sample identification number;
- location and condition of storage;
- date and time of each removal of, and return to storage;
- signature of person removing and returning the sample;
- reason for removal from storage; and
- final disposition of sample.

All logbooks, labels, data sheets, tracking logs and custody records should have proper identification numbers and be accurately filled out. All information should be written in indelible black ink. Corrections should be made by drawing a line through the error and entering the correct information. Corrections should be initialed and dated. Accuracy of all data reductions and transcriptions should be verified at least twice. All samples and documents should be properly stored within the laboratory until the client authorizes their removal. Security and confidentiality of all stored material should be maintained at all times. Before releasing analytical results, all information on sample tags, data sheets, tracking logs, and custody records should be cross-checked to ensure that data pertaining to each sample are consistent throughout the record.

Originals of the following documents should be sent to the client:

- chain of custody record,
- sample tracking logs,
- data report sheets, and
- quality control records.

Copies of all forms should be retained by the laboratory in case originals are lost in transit.

6.2 Chain of Custody Procedures

Many projects will require chain of custody procedures be followed if the project comes under regulatory scrutiny. Chain of custody may be defined as *an unbroken trail of accountability that ensures the physical security of samples, data, and records* (ANSI/ASQC, 1994). Field chain of custody procedures should be followed from the time a sample is collected until it is relinquished to the analytical laboratory (either in person or to a shipper). A chain of custody form should be initiated when the first sample is collected and updated continuously through the sampling event. A new chain of custody form should be prepared for each day of field sampling. Information to be entered on the chain of custody form should include sample number, date and time of sampling and names of all sampling personnel. The form may also include type of sample container and requested analyses.

A sample is considered to be “in custody” when in the possession or view of the sampling personnel or in a secured area. A custody seal should be placed on the sample cooler when it is not in the custody of a member of the sampling team.

When samples are relinquished, either to the laboratory or for shipment, the chain of custody form must be completed by the sample deliverer. It should include the printed and signed name of the deliverer, the organization that person represents, date and time of sample relinquishment, and method of shipment, if appropriate.

6.3 Holding Times and Conditions

Observance of proper holding times and conditions during sample shipment and prior to laboratory analysis is critical to obtaining quality data from a sampling effort. Immediately after collection, samples should be stored in refrigerators (if available) or ice filled, insulated coolers to maintain an ambient temperature of approximately 4°C until receipt by the analytical laboratory. Sample holding times and conditions for specific matrices and analyses are outlined in Tables 2, 3 and 4.

7. DOCUMENTATION AND REPORTING

This section provides guidance for documenting sampling and data gathering activities. The documentation of field activities provides important project information and data that can act as support to data generated by laboratory analyses. Project data validation may require reporting field data to verify sample identification, sampling locations, correct sampling techniques. It may also be necessary to validate results of field analyses and measurements.

7.1 Field Notes

Field notes should be maintained for all field activities, whether the collection of samples or the gathering of environmental data. Field notes should be kept on water-resistant paper and all field documentation should be recorded in indelible black ink. Information recorded in field notes for water samples may include, but not be limited to:

- name of recorder;
- sample and station number;
- data or sample station locator information;
- sample elevation (water depth of the sampler bottle);
- date and time of sample or data collection (all times should be recorded for multiple sampler deployments);
- ambient characteristics such as temperature, salinity, transparency, pH, and Eh (redox); and
- ambient climatological characteristics such as air temperature, cloud cover, and precipitation.

The following are examples of notes that may be added for sediment samples:

- sample elevation (water depth above the surface of the sediment);
- sampling interval (i.e., 0 to 10 cm);
- positioning information required to calculate the location of the station;
- physical characteristics such as gross particle size distribution, debris, odor or evidence of contamination such as a visible sheen or discoloration;
- record of splits, duplicates and subsamples taken;
- physical measurements such as particle size, interstitial pore water salinity, pH, or Eh (redox); and
- tidal information.

Other information that may be recorded in field notes includes sampling methodology and any deviations from established sampling protocols. Additional anecdotal information pertaining to observations of unusual sampling events or circumstances may be recorded in field notes. A field book should be unique to the project or, at the very least, to a class of field events, such as marine sediment sampling. It is also advisable to keep record of all personnel involved in each sampling event, including the time each individual boarded and departed the research vessel.

For sediment coring operations, a core splitting data sheet should be completed for each core sampling station. The core splitting data sheet is completed when the core is sectioned and samples split. The core splitting data sheet should include:

- project name;

- core identification name or number;
- sampling date and core splitting date and time;
- personnel involved in core splitting;
- individual sample numbers split from the core;
- core compaction calculations;
- depth range of sample sections split from the core;
- sample observations such as color, debris, gross particle size distribution and odor for each sample section; and
- storage conditions from time of receipt at laboratory until splitting (i.e. refrigerated or frozen).

The analytical laboratory can be a source of valuable information for observations made during the preparation of a sample aliquot for analysis. In many cases it may be advisable to provide the analytical laboratory with a project form to record any observations they might make during the analytical process. This form would be included with the analytical results as part of the deliverable package.

7.2 Field Analyses and Field Instrument Calibration Records

Field analyses frequently provide project information that is as important as data generated by laboratory analyses. Results of field analyses or measurements should be recorded in a manner that provides easy identification of the information as analytical results. This information should be kept in a section of a field book separate from general field notes. In addition to field analytical results or measurements, field instrument calibration records provide critical information to allow data users to judge the validity of field measurements and analyses. All information should be recorded in indelible, black ink and errors should be crossed out with a single line and initialed and dated by the data recorder.

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10. APPENDIX A - HEALTH AND SAFETY

Certain projects will require preparation of a site-specific Health and Safety Plan (HSP) as part of the project planning process. A HSP is required for sediment sampling at sites listed under one or more of the following:

- Model Toxics Control Act (MTCA),
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and
- Sediment Management Standards (SMS).

A HSP is also required for any other project in an area that is known to be contaminated by toxic materials. Requirements for HSPs are provided by the Department of Labor and Industry and detailed in WISHA/OSHA regulations.

All members of a sampling team working at a hazardous site must receive 40 hours of hazardous waste operations (HAZWOPER) training as prescribed by OSHA Regulation 29 CFR 1910.120, and at least one member must receive supervisory training. Employers must make a medical monitoring program available to all crew members conducting sampling operations at hazardous sites. All sampling team members must read and understand the contents of the HSP prior to the commencement of field work, and verify such by signature on the original HSP document.

10.1 General Health and Safety

Since a site-specific HSP is not prepared for all sampling projects, the following general health and safety guidance is provided.

- All crew members should receive annual vessel safety training which will include proper chain of communication, equipment operation and safe boating practices.
- Sampling personnel should wear, at a minimum, chemical-resistant gloves when coming in contact with contaminated sediment.
- No eating, drinking or use of tobacco products should be allowed during sampling operations.
- All accidents (or near-accidents), including instances of possible exposure to health-threatening elements, should be reported to the respective supervisor within 24 hours of occurrence.

10.2 Health and Safety During Sampling Activities

Marine sampling can be inherently dangerous, and proper precautions need to be taken. The physical hazards unique to sampling equipment, sampling operations, general vessel safety, and chemical hazards are described in Sections 10.2.1 through 10.2.4.

10.2.1 Hazards Associated with Sampling Equipment

There is a large variety of marine sampling equipment in use today and each has the potential for causing serious injury. Many types are heavy, ranging from under 50 pounds for a small sediment grab or plankton net to up to 2,000 pounds for a large Ewing piston corer. Unless the equipment is secure on deck or fully deployed and submerged, care must be taken to avoid crushing or other impact-related injuries from the handling of this gear.

In addition to being heavy, coring equipment can also be dangerous in that it is usually weighted toward the top end, making its handling more awkward. Also, an appreciable amount of vertical clearance is usually required to clear the gunwale during deployment and retrieval, which in turn can increase the risk of uncontrolled lateral motion unless suitable tethers are used.

A typical box corer is fairly heavy (from 700 to 900 pounds) and is also both tall and wide at the base. At least 100 square feet of deck area is required to safely manage this equipment. Good foot protection is mandatory.

With impact coring, which uses concussion as the primary means for driving the core tube, personnel may have the potential hazard of fragmentation, breaking of high-pressure lines and danger of fast-moving parts to contend with. Ear protection may also be necessary.

Essentially all types of sediment grabs (or snappers) utilize their own weight, some type of tensioning device or other form of mechanical advantage to actuate the sampler upon contact with the bottom. Care must therefore be taken to minimize the risk of accidental or premature closure while handling. Once a grab is armed or cocked, the safety device on the tripping mechanism should be in place until the sampler is clear of the rail and over the side.

In general, all sampling equipment uses the same type of marine hardware to attach to the appropriate lifting device. Periodically, all connections (e.g., cabling, shackles, pins, swivels etc.) should be inspected to ensure the integrity of all points along the sampling assembly.

10.2.2 Safety During Sampling Operations

A sampling device is least secure while suspended in the air during the transitional period between the deck of a vessel and the surface of the water; a pitching and/or rolling deck during rough weather will aggravate this situation. Care must be taken to ensure that sufficient restraining lines or other devices are in place to meet these conditions.

Because of the increased potential for damage or injury, all personnel on deck and in the wheelhouse must be notified before a sampling device leaves the deck during deployment or breaks the surface upon retrieval. If the winch operator is remotely located from the scene of operations, a clear system of signals must be established between the lead deck person and the winch operator, usually via hand signals or electronic communication.

Hard hats, gloves and steel-toed boots should always be worn if the potential for serious injury exists when working topside. OSHA requires that hard hats be worn when working beneath suspended equipment, or when the potential of injury to the head exists due to lateral impact.

All crew members should have a suitable level of seamanship skills, based upon their level of responsibility. Listed below are some of the items related to seamanship and gear-handling that, when overlooked, have been known to cause serious accidents on board ship.

- A capstan is potentially more dangerous than a winch drum, as the wraps are not enclosed and could instantly slip off the end if not handled properly.
- If a hydraulic hose fails, winches can free-wheel and load-bearing rams can collapse under a load

unless backed up with balance-check valves.
- Different kinds of line and wire rope have different characteristics which may not be suitable for all applications (e.g., nylon is 25 percent stronger than polypropylene, but it is much more elastic and can be lethal if parted under a strain; polypropylene will float, making it less susceptible to propeller entanglement).
- An eye splice over a thimble will only cause a 5 percent reduction in line strength, but a knot (depending on type) can reduce the strength in a line by as much as 55 percent due to unequal strain on the fibers (a line will usually break under a strain at that point where it is forced to bend).
- Theoretically, the longer a line under a strain, the weaker it is when compared against its rated breaking strength (the chances are statistically greater of encountering a section weaker than the last as line length increases).
- The recommended working load-to-breaking strain for wire rope and line is typically 1 to 5. If the load ever exceeds 75 percent of the breaking strength, permanent damage could result, which can lead to unexpected breakage.
- Topside operations may be more dangerous on larger ships than smaller vessels because it is harder to keep track of safety concerns when activities are spread over a larger area of deck.
- Crew members should always stand clear of slack or looped line laying on deck to avoid entanglement. A sudden strain on slack line can entrap arms and legs; personnel may be severely injured or carried overboard.

Inclement weather may introduce additional hazards. Heavy equipment can be much more difficult to manage, and footing may become more unsure due to slippery decks and/or increased vessel motion, and the risk of falling overboard may increase. WISHA requires that all railings be a minimum of 36 inches in height and OSHA requires that an approved life vest be donned when working over the water or if there is an increased risk of falling overboard. Vessel accommodations should be able to provide relief to crew members in case of cold or heat stress.

10.2.3 General Vessel Safety

To ensure adequate preparation for emergencies that may possibly arise, the following safety equipment should be required on all research/sampling vessels:

- one Coast Guard approved personal floatation device for each crew member (waterproof lights must be included for nighttime operations);
- at least one throwable floatation device;
- an emergency life raft with accessories (optional);
- at least one emergency self-actuating radio beacon;
- two very high frequency (VHF) marine radios (Coast Guard channel 16 and Vessel Traffic System channel 14 both need to be monitored);
- a cellular telephone (desirable);
- navigation lights;
- an anchor and line;
- three signal flares (for nighttime);
- three orange smokes (for daytime);
- radar (for reduced visibility);
- bilge pumps;
- fire extinguishers;

- a horn;
- reach pole or gaff;
- an accessible, clearly-labeled, fully stocked first-aid/CPR kit; and
- an accessible, clearly-labeled eye wash kit.

Protective gear for sampling personnel should include:

- a hard hat,
- steel-toe rubber boots,
- chemical-resistant gloves (e.g., Nitrile),
- safety glasses,
- respiratory protection,
- rain gear (if necessary), and
- hearing protection (if safe noise levels are exceeded).

Some HSPs may require that a safety officer be assigned to oversee sampling operations. However, it is important to note that the ship's captain has the ultimate responsibility and authority (as recognized by the U. S. Coast Guard) to immediately override the authority of all other on board personnel, especially where the general welfare of ship and crew are concerned.

10.2.4 Chemical Hazards

In some areas, contact with marine sediment may present a health hazard from chemical and/or biological constituents of the sediment. Possible routes of exposure to chemical/biological hazards include **inhalation, skin and mucous membrane absorption, ingestion, and injection**. Potentially hazardous chemical/biological sediment constituents may include hydrogen sulfide, mercury and other heavy metals, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, solvents, and various types of bacteria and viruses. Other potentially hazardous substances may include chemicals used as sample preservative agents or sampler decontamination agents.

Crew members should exercise caution to avoid coming into contact with contaminated sediment during sampling operations. Protective equipment should include chemical-resistant gloves, safety glasses or goggles, and protective clothing such as rain gear. Crew members should exercise good personal hygiene after sampling and prior to eating or drinking.

Exposure to airborne contaminants can be greatly reduced if the vessel steams to windward in a way that minimizes risk to the sampling crew from exposure to volatiles. Having respirators on hand is advisable to reduce exposure to volatile fumes that may be present when mixing large quantities of sediment or using a solvent rinse during equipment decontamination. The use of an air monitoring instrument is recommended when airborne contaminants are suspected in a sampling area or the sampling area has poor ventilation, such as under piers or docks.